California Environmental Protection Agency

Air Resources Board

SOP MLD 057

STANDARD OPERATING PROCEDURE FOR THE DETERMINATION OF 1,3-BUTADIENE AND BENZENE IN AMBIENT AIR BY CAPILLARY COLUMN GAS CHROMATOGRAPHY WITH PHOTOIONIZATION DETECTOR

Engineering and Laboratory Branch
Monitoring and Laboratory Division

First Approved Date of SOP: January 1, 1999
Approval Date of Last SOP Amendment: January 1, 1999
Revision Number: 1.0

Table of Contents

List of Tables

List of Figures

SOP MLD 057

STANDARD OPERATING PROCEDURE FOR THE DETERMINATION OF 1,3-BUTADIENE AND BENZENE IN AMBIENT AIR BY CAPILLARY COLUMN GAS CHROMATOGRAPHY WITH PHOTOIONIZATION DETECTOR

1.0 SCOPE

This document describes the procedures followed by Monitoring and Laboratory Division (MLD) staff to analyze 1,3-butadiene and benzene by Gas Chromatography (GC) in ambient air samples collected from the California Toxic Monitoring Network. The method was developed by staff of the Engineering and Laboratory Branch (ELB), Organics Laboratory Section (OLS). This Standard Operating Procedure (SOP), MLD057 Revision 1.0, supersedes SOP MLD051 Revision 3.0 for determining 1,3-butadiene and benzene concentrations in ambient air. The new SOP includes a multi-point calibration procedure for quantitation of butadiene and benzene. Minor changes were also made in the GC relay program, which affects the post-injection system configuration.

2.0 SUMMARY OF METHOD

Ambient air is collected in a SUMMA polished stainless steel canister using a XonTech 910A sampler. The sampling procedure for Toxics samples is detailed in the Air Resources Board Quality Assurance Manual, Volume II, Appendix Q. All the operational procedures and sampling conditions for each sample are documented in the field. A record of this information is sent back to the OLS along with the sample. Upon receipt, the sample canister pressure is measured with a calibrated external pressure gauge. This information and particulars of the collection are documented in the laboratory. The sample is then analyzed according to the SOP in the laboratory.

An ambient air sample is introduced into the analytical system from a pressurized canister through stainless steel or Teflon tubing with the aid of a mass flow controller (MFC) and a vacuum system. A digital readout attached to the MFC provides a visual indication of the proper sample flow during sampling. Automated sampling of up to 16 canisters can be accomplished using the system's multi-position stream selector valve.

The sample passes through a Nafion™ dryer to remove moisture from the gas stream. It is trapped on a cryotrap at -150 degrees centigrade (ºC). At this temperature, the desired components are solidified, while fixed gases, such as nitrogen (N_2), oxygen (O_2), and carbon dioxide (CO_2), and methane (CH_4) pass through the cryotrap to the vent. The system is purged with ultrapure N_2 to flush sample remaining in the tubing or valving on to the cryotrap, and to remove any excess light impurities. The cryotrap is isolated and rapidly heated to 125^{o}C, followed by injection of the sample onto a DB-VRX capillary column. After a short hold at 125^{o}C, the trap temperature is raised to a final temperature of 190^{o}C.

The sample mixture is separated into individual components by their interaction with the capillary column stationary phase, using temperature-programmed gas chromatography. The components eluting from the column are detected by a Photoionization Detector (PID). The target analytes, 1,3-butadiene and benzene, are subsequently identified and quantified. Routine identification of a component in a sample as 1,3-butadiene or benzene is based upon the relative retention time. The initial positive identification of a peak under the method conditions requires the use of a gas chromatograph/mass spectrometer (GC/MS) system.

3.0 INTERFERENCES AND LIMITATIONS

3.1 Although preliminary studies have shown that 1,3-butadiene and benzene can be considered stable in stainless steel canisters, every effort must be made to analyze the sample as soon as possible. Extreme care must be taken to prevent contamination during sample collection, transportation and subsequent analysis.

3.2 Since the retention time of an analyte is one of the keys for identifying a component in gas chromatography, the retention times of the GC system must be reproducible.

3.3 Compounds with similar GC retention times may not be completely separated or may co-elute. This can cause misidentification or inaccurate quantitation.

3.4 Although the analytical system separates and detects other saturated and unsaturated hydrocarbons, only 1,3-butadiene and benzene are addressed by this procedure.

3.5 No more than 10 samples should be run consecutively without system recalibration due to the continuous reduction in PID lamp signal.

3.5.1 The loss of PID lamp signal and increased background noise can be caused by the deposition of high boiling compounds on the PID lamp lens. To reduce sample deposition, the detector temperature can be increased, but it should not exceed the maximum recommended operating temperature of 280°C. Operating at temperatures greater than 250°C reduces the life of the internal Vespel seals. It can also **increase** background noise.

3.5.2 When the signal decreases substantially, the lamp should be cleaned or replaced. The PID lamp may be cleaned with PID lamp polishing compound followed by rinsing with water or methanol.

3.5.3 References:

"Model 703 Photoionization Detector (PID)", Operations Manual, 116439 M, Revised March 1992, Tremetrics

"Photoionization Detector", 03-9141118-00, July 1986, Varian

3.6 Daily baseline shifting, or the appearance of broad, extraneous "ghost" peaks, may be caused by high boiling compounds being trapped on the column. The column should be baked out prior to each set of analytical runs to remove these contaminants. The bake out temperature should not exceed the column's maximum operating temperature of 260 °C.

3.6.1 Reference:

"1996/1997 Catalog and Technical Reference", J & W Scientific, Inc.

3.7 Vinyl chloride is monitored by this method but is not reported due to the low ambient concentrations.

4.0 APPARATUS

4.1 A Varian Model 3400CX gas chromatographic system, with:

4.1.1 An automated sampler, consisting of an 8134 multi-position Stream Selector Valve (SSV) and a Mass Flow Controller (MFC) with a Control/Digital Readout module.

4.1.1.1 The MFC is mounted downstream of the SSV and the cryotrap to eliminate any contamination and to reduce dead volume in lines from sample trap.

4.1.1.2 The MFC is typically rated at 100 cm^3/min at 100% full scale. The flow rate is set as a percentage of full scale. For example, a flow rate of 50 cm^3/min corresponds to a setting of 50% full scale.

4.1.1.3 The Control/Digital Readout module is set to the side or on top of the GC.

4.1.1.4 A rotometer is mounted on the GC, between the MFC and the vacuum source, to allow visual confirmation of flow.

4.1.2 A Cryogenic Pre-Concentrator, containing a 150 microliter (µL) empty nickel tubing cryotrap.

4.1.3 A Photoionization Detector (PID), using a 10.2/10.6 eV lamp.

4.1.4 Digital flow controllers and pressure regulators installed in a heated pneumatics compartment.

4.1.4.1 A pressure regulator set in parallel with the carrier gas flow controller to minimize flow upsets during valve switching.

4.1.4.2 The digital flow controllers are calibrated to deliver helium (He) flows from zero to 100 cm^3/min, $\pm$ 3%, with an inlet pressure of 80 psi.

4.1.5 Analog pressure gauges and digital Electronic Pressure Readouts (EPR) for use in gas monitoring and diagnosing problems with the flow system.

4.2 A canister sampling manifold for connecting canisters to the automated sampler, using appropriate tubing and fittings.

4.2.1 Examples of tubing size and material are $^1/_8$ inch Teflon tubing, $^1/_{16}$ inch stainless steel tubing, $^1/_{16}$ inch nickel tubing, or $^1/_{16}$ inch glass lined stainless steel tubing.

4.2.2 Canisters are connected to the manifold, and the manifold is connected to the automated sampler's SSV.

4.3 A J&W DB-VRX 75 m by 0.45 mm i.d., with 2.55 µm film thickness, fused silica capillary column.

4.3.1 Reference:

"1996/1997 Catalog and Technical Reference", J & W Scientific, Inc.

4.4 A continuous, self-regenerating, in-line Nafion™ sample dryer, from Perma Pure Inc.

4.5 A Varian GC Star Workstation, which includes an Intel compatible PC, up to four (4) Varian serial communication cards, and Varian Star Chromatography software.

4.5.1 The Workstation is used for GC system configuration, sample file lists, sequence lists, and method building.

4.5.2 The serial communication cards provide digital communication with the GC.

4.5.3 Reference:

"Varian GC Star Workstation Manual" by Randall Bramston-Cook.

4.6 A Perkin-Elmer (PE) Data Station, including an Intel based PC and PE-Nelson 2700/Turbochrom™ Chromatography software, and one or more PE-Nelson Model 970 Analog/Digital Converters.

4.6.1 The Data Station is used for storage of raw data files and the subsequent processing of the raw data to produce qualitative/quantitative data.

4.6.2 The PE-Nelson Model 970 Analog/Digital Converter converts the GC's analog detector signal to digital data and stores the digital raw data until it is transferred to the PE Data Station.

4.7 Stainless steel SUMMA passivated canisters for sample collection and standard preparation.

5.0 REAGENTS

5.1 A system blank, consisting of zero air, ultrapure air or Grade 5 ultrapure N_2, in a SUMMA passivated canister that has been humidified with 150 µl of HPLC grade water.

5.2 A certified National Institute of Standards (NIST) hydrocarbon standard mixture containing all analytes of interest. This standard should be slightly higher in concentration than the typical sample and must be within the linear dynamic range of the GC system. Table 7 lists the NIST Standards associated with the analysis of 1,3-butadiene and benzene.

5.3 A control sample containing 1,3-butadiene and benzene at concentrations within the calibration range of the GC System. Table 7 lists the Control Standards associated with the analysis of 1,3-butadiene and benzene.

5.4 One high pressure gas cylinder of Grade 5 or better He for use as the GC column carrier gas.

5.5 Three high pressure gas cylinders of Grade 5 or better N_2.

5.5.1 One cylinder supplies gas to operate the pneumatic valve actuators and provides clean blank gas to port number one on the SSV. A separate gas cylinder is recommended for the valve actuators to minimize spikes on the PID from pressure pulses when valves are turned. He can be used for this purpose if necessary.

5.5.2 One cylinder supplies dry gas to the Nafion™ dryer.

5.5.3 One cylinder provides makeup gas to the PID.

5.6 A dewar of liquid nitrogen (LN_2) for cooling the cryotrap and the GC column oven.

6.0 INSTRUMENT CONFIGURATION AND PARAMETERS

6.1 The analytical system's gas flow and automation configurations are shown in Figure 1 through Figure 8. A complete listing of the current Varian Star Workstation method, which includes all of the GC setpoints controlled by the Workstation, is given in Appendix I.

6.2 GC Injector [Cryotrap]

6.2.1 In this system, the GC injector is the cryotrap. The cryotrap utilizes a low trap volume ($\leq$150 µL) and a rapid heating/cooling cycle (-150^{o}C to 125^{o}C in less than 0.80 minutes) for efficient transfer of sample to the capillary column.

6.2.2 The set temperature for the GC Injector does **not** correspond to the actual temperature of the injector. This results from a hardware limitation in the Varian GC's on-board alphanumeric display. The actual temperature is obtained by using the Injector Temperature Conversion chart given in Figure 9. The actual temperature values, as given in Appendix I, are from that chart.

6.2.3 GC Auxiliary

In this system, the GC Auxiliary oven is used to maintain the three Gas Sampling Valves (GSVs) at a constant temperature.

6.3 GC Column Oven

6.3.1 This oven contains the chromatographic column. Reproducible temperatures in the column oven under isothermal and programmed conditions are very important to producing reproducible retention times for components. This is critical for the qualitative aspects of the method.

6.3.2 The oven temperature conditions are directly involved with the interaction between all components and the stationary phase of the column. The temperature program can change the resolution between components, which affects the qualitative and quantitative aspects of the method.

6.3.3 The GC Column A Parameters and the GC Column B Parameters in the method DO NOT alter or control any setpoints in the GC. Listing a column as installed allows the pressure readings from the digital Electronic Pressure Readouts (EPR) to be displayed on both the GC's on-board alphanumeric display and the Star screen of the associated Workstation.

6.4 GC Detector(s)

6.4.1 The instrument has both a PID and an ECD installed in a series configuration. The ECD is not used for this analysis.

6.4.2 The Attenuation parameter in the method has no effect on the signal output to either the Star or PE-Nelson Chromatography Data Acquisition systems.

6.5 GC Autosampler

This section of the method designates the 8134 multi-position Stream Selector Valve as the input source for samples into the system.

6.6 GC Relays [Post Injection Relay Time Program]

This portion of the method contains the time setpoints for activating relays, which in turn control the various valves used in the GC. These actions take place after the Pre-Injection Program (PIP), which is described below.

6.7 GC Stripchart

There is no stripchart recorder attached to the instrument. Printed output is obtained through the Star GC Workstation and the Star Chromatography software.

6.8 GC Gas Flows

The current gas flows and regulator pressures are shown in .

6.9 Mass Flow Controller

The sample volume for the column injection is fully automated by the use of 8134 SSV Relay Time Program that is part of the Varian GC Star Workstation software. The function of the valves in the Varian 3400CX GC system are shown in Table 1. The valve actuators and their corresponding degrees of rotation are listed in Table 2.

The setpoint for the MFC is shown in Appendix II.

7.0 DAILY OPERATION

7.1 Initial Setup

7.1.1 Canister samples are connected to the autosampler using appropriate tubing and fittings. The sample canister valves are opened and the canister pressure gauge is monitored to assure a leak-free connection.

7.1.2 The GC system configuration profile, sample file list (.smp), sequence list (.seq) and method file (.mth) are set up on the Star Workstation. Appendix I has further details.

7.1.3 The data acquisition sequence list (.seq) and method file (.mth) are set up on the PE Data Station. Appendix III has further details.

7.1.4 The sample flow rate setting is confirmed on the MFC's Control/Digital Readout module. The sample volume is determined as the product of the trapping time, in minutes, times the flow rate, in cm^3/min, set on the MFC. For example:

Trapping Time:	8.0 minutes
Flow Rate:	50.0 cm^3/min
Volume:	8.00 min x 50.0 cm^3/min = 400 cm^3

Confirmation of the actual flow rate can be done with an external flow meter.

7.2 Sample Preconcentration and Analysis

7.2.1 Samples are introduced onto the cryotrap under control of the Pre-Injection Program (PIP), an automated relay time program setup in the sample list on the Star Chromatography Workstation. The PIP valve configurations and events are shown in Figure 1 through Figure 5. The PIP times, relay # and status, and events are set in the sample list file (.smp) as shown in Table 3: Pre-Injection Program Times, Relay #s, and Status.

7.2.2 At the end of the PIP, control of the analysis is passed to the GC Program. It controls heating of the cryotrap through the GC Injector Program, and the subsequent direct transfer of the trapped sample onto the GC column through the GC Relay Program. The GC Relay Programs valve configurations and events are shown in Figure 6 through Figure 8. The GC Relay Program times, relay # and status, and events are set in the method file (.mth) as shown in Table 4: GC Relay Program Times, Relay #s, and Status.

7.3 Samples

7.3.1 A system blank is analyzed prior to calibration standards, controls and samples to evaluate the system cleanliness. System blanks are also be run after samples which contains high concentrations (>4 ppb of 1,3-butadiene or >20 ppb of benzene) to detect and eliminate possible carry-over.

7.3.2 Daily calibration standards are analyzed after the system blank, prior to controls or samples.

7.3.3 A control sample is analyzed after the system blank and calibration standards, prior to ambient air samples, in order to evaluate the accuracy of the calibration and the overall performance of the system, as shown in Table 4. The control sample contains only 1,3-butadiene, vinyl chloride, and benzene in N_2. The daily results of these control standards must fall within the control limits as defined in the Method Quality Control Report.

7.3.4 Ambient samples are analyzed using the same sample volume as used for the calibration standard and control sample. A smaller volume is analyzed for samples containing concentrations of 1,3-butadiene or benzene that exceed the calibrated range of the analysis. Smaller volumes are obtained by reducing the pre-concentration time while keeping the MFC setpoint constant.

7.3.5 Duplicate analyses are performed on 10% of all ambient samples analyzed. The relative percent difference of the duplicate analyses, for samples with 1,3-butadiene and/or benzene concentrations greater than 5 X Limit of Detection (LOD) are recorded and included in the method quality control report.

8.0 DATA ANALYSIS

8.1 After data acquisition, the raw data files (.raw) collected on the PE Data Station are processed by the Turbochrom™ software to produce result files (.rst). The result files contain the integrated chromatographic peak areas and retention times.

8.2 Chromatographic peaks in the result files for calibration standards are qualitatively identified based on retention times and analyst experience. After analyte identification, the calibration standard result files are used to calibrate the Turbochrom™ method for both retention time and concentration. The latter is based on the peak areas and the known analyte concentration in the standards.

8.3 After calibration of the method, chromatographic peaks in blank, control, and ambient sample result files are qualitatively identified based on relative retention times and are quantified using the calibration curve in the method.

8.4 A typical chromatogram of an ambient air sample is shown in Figure 10.

9.0 QUALITY CONTROL

9.1 System Blank

A system blank must be analyzed before any standard or sample is run. The system blank must not contain 1,3-butadiene nor benzene at greater than two times the LOD in order to validate any subsequently analyzed samples. Trip blanks, if available, are analyzed like samples and their results are documented and evaluated.

9.2 Multipoint Analysis Verification

A multipoint analysis must be performed every year to verify the precision and the calibration working range. This is done by analyzing at least five simulated concentration levels of the NIST standard in triplicate.

A multipoint calibration is also required under the following conditions:

a.) When the column is changed.

b.) When major maintenance is performed.

c.) When there is a change in the matrix or a reagent.

Typical calibration working range determinations are presented in Figure 11 and Figure 12.

9.3 Limit of Detection (LOD) Verification

The LOD must also be verified on a yearly basis, or when the same conditions as listed under the multipoint calibration verification occur. This is done by analyzing a minimum of seven (7) replicates of the lowest standard concentration used for calibration. This concentration must be no more than five (5) times the estimated LOD.

The LOD is estimated using the following equation, as specified in Section 9.1 of the ELB Quality Control Manual

$$LOD = t_{(n-1,\ 1-á\ =\ 99\%)} \times S$$

$t_{(n-1,\ 1-á\ =\ 99\%)}$ = student's T-distribution value at n-1 degrees of freedom

S = standard deviation

The LOD determinations are presented in Table 5.

The published LODs for this method are:

1,3-butadiene.................................0.04 ppbv
benzene...0.2 ppbv

All subsequent LOD verifications must be equal to or less than these values.

9.4 Daily Calibration

A multi-point 2nd order calibration curve, forced through zero, is calculated for each analytical run from the calibration standard analyses performed during that run. A minimum of three standard concentrations are necessary to construct this type of standard curve. All calculations to produce this curve are done by the PE Turbochrom™ Data Analysis software. The Turbochrom™

method is updated after every run with the new calibration information. The method, calibration curves, the equation coefficients, and the correlation coefficients can be printed for a hardcopy record.

To be acceptable, the 2nd order correlation coefficient must be 0.98 or better.

9.5 Control Standard

A standard mix, containing 1,3-butadiene and benzene at concentrations within the calibration range of the GC System, is chosen to be the control standard. Analysis results of 1,3-butadiene and benzene in this standard are recorded and used to generate control charts. At least 20 data points are needed for the initial set of control limits, and any subsequent adjustment of these limits. Typical Control Charts are shown in Figure 13.

The upper and lower control limits are set at ± three times the standard deviations (SD) from the average. The upper and lower warning limits are set at ± two times the SD from the average. If the % relative standard deviation (%RSD) of the control set is less than 5%, the %RSD is set to 5% and the SD is revised accordingly. The control are then set using the revised SD. This provides minimum upper and lower control limits of ± 15 % and upper and lower warning limits of ± 10 %. A typical dataset used for calculating control limits is given in Table 6.

Control standard results must be within the established control limits for sample analyses to be valid.

9.6 Method Precision

Sample precision is measured by the analysis of ambient duplicate samples and the analysis of ambient collocated samples. The frequency of duplicate analyses is 10% of the total ambient samples analyzed. Control limits for the percent difference (PD) of the duplicate sample analyses is the same as the control limits for the Control Standard.

The PD for collocated sample analyses is used to evaluate method precision including both the sampling and analysis. The PD for co-located sample analyses should be within ± 25%.

9.7 Method Accuracy

Method accuracy is assessed by periodically analyzing other standard reference materials, if available. The results of replicate analysis of these materials must be within ± 20% of their reported values.

Audit samples, provided by either MLD's QM&OSB's Quality Assurance Section, or another outside source are analyzed when available. They can also be used for assessing method accuracy.

Table 1: Function of Valves for Varian GC 3400CX System

Valve #	Function	Relay Event	Rotation
1	Int. Std/Spike Flow Off	- 1	On
	Int. Std/Spike Flow On	+1	Off
2	Trap In Series	-4	Counterclockwise
	Trap Isolated	+4	Clockwise
3	Purge Lines – Sample Flow Off Inject Internal Standard/Spike	- 3	Counterclockwise
	Sample Flow On Load Internal Standard/Spike	+3	Clockwise
4	Inject Trap	- 2	Counterclockwise
	Load Trap	+2	Clockwise

Table 2. List of Valve Actuators for Varian GC 3400CX System

Relay #	# of Valve Ports	Rotation	Description
2	4	90º	Series/Bypass
3	10	36º	GSV Sample on/off
4	6	60º	GSV

GSV: Gas Sampling Valve; Sx: Sample

Table 3: Pre-Injection Program Times, Relay #s, and Status

Time (minutes)	Relay # & Status	Events
0.00	-1-2-3-4	All valves are off (-). The sample flow is blocked and N_2 purge gas is allowed to flow through the MFC to the vent. He carrier gas is directed through the cryotrap to the column.
0.01	-1-2**+3**-4	Valve #3 is turned on **(+3**). This allows the sample to flow through the mass flow controller to the vent and purge the lines with new sample. He carrier gas is directed through the cryotrap to the column.
1.00	-1**+2+3**-4	Valve #4 is turned on (**+2**) and Valve #3 remains on (**+3**). The sample flow is directed through the cryo-trap, then the MFC to vent. This starts sample loading. He carrier gas continues through the col-umn.
9.00	-1**+2**-3-4	Valve #4 remains on (**+2**) and Valve 3 is turned off (-3). This terminates sample loading. The sample flow is blocked, allowing N_2 to purge the intercon-necting lines and their contents onto the cryotrap. He carrier gas continues through the column. ***Note: The sample volume is varied by control-ling the actions of Valve #3.***
9.10	-1**+2**-3**+4**	Valve #4 remains on (+2) and Valve #2 is turned on (**+4**). The cryotrap is isolated. N_2 purge gas is al-lowed to flow through the MFC to the vent. He car-rier gas continues through the column. ***Note: This ends the pre-injection program events.*** ***<u>The activation of Valve #4 starts PE Nelson data acquisition.</u>***

Table 4: GC Relay Program Times, Relay #s, and Status

Time (minutes)	Relay # & Status	Events
0.00	-1**+2**-3**+4**	Valves #4 and #2 remain on (**+2+4**). The cryotrap is isolated. N_2 purge gas is allowed to flow through the MFC to the vent. He carrier gas continues through the column. **Note: This is exactly the same state as the last step of the PIP. In fact, the last step of the PIP overwrites the first step of the GC Relay Program.**
0.02	-1-2-3**+4**	Valve #2 remains on (**+4**) and Valve #4 is turned off (-2). The cryotrap is isolated and He carrier gas is directed through the column. Cryotrap pre-heating in started.
1.50	-1-2-3-4	Valve #2 is turned off (-4). He carrier flow is directed through the cryotrap, then to the MFC and the vent. This starts sample injection onto the column. **Note: The system remains in this state throughout the run. This relay state is exactly the same as the first step in the PIP.**

Table 5: Estimated Limits of Detection

August 15, 1998

		BUTADIENE			BENZENE	
RUN	STANDARD	Area Counts	ppb		Area Counts	ppb
7	AAL67810	561	0.04		5719	0.25
8	AAL67810	497	0.04		5186	0.23
9	AAL67810	430	0.03		5521	0.25
10	AAL67810	481	0.04		5438	0.24
11	AAL67810	420	0.03		5222	0.23
12	AAL67810	411	0.03		5220	0.23
13	AAL67810	443	0.03		5173	0.23
	Avg.	463.29	0.03		5354.14	0.24
	Std dev	53.43	0.01		209.97	0.01
	% Rsd	11.53	15.59		3.92	4.01

3.14 x Std Dev		0.02			0.03
n =		7			7
Established LOD		0.04			0.20

Table 6: Precision Measurements of 1,3-Butadiene and Benzene

Control Values for NLB57

Established on July 14, 1999
Control Gas CC113563/Calibration ALM29258

	Analysis Date	Butadiene	Benzene
	July 14	0.988	3.462
		0.989	3.505
		0.982	3.538
		0.981	3.547
		0.989	3.565
		0.963	3.562
		0.980	3.530
		0.973	3.558
		0.975	3.540
		0.980	3.538
		0.963	3.531
		0.965	3.596
		0.965	3.589
		0.956	3.585
		0.957	3.605
		0.945	3.547
	July 20	0.970	3.342
		0.964	3.350
		0.971	3.377
		0.968	3.551
		0.966	3.534
		0.969	3.517
	July 21	0.972	3.528
		0.958	3.503
		0.961	3.511
	July 26	0.973	3.288
		0.980	3.394
		0.973	3.409
		0.955	3.590
		0.956	3.569
	July 28	0.980	3.462
		0.991	3.458
		0.965	3.578
	Mean	0.97	3.51
	Std Dev.	0.011	0.081
	RSD%	1.2	2.3
PRECISION	Assigned RSD	5.0	5.0
	Assigned Std	0.049	0.175
	# of Observations	33	33
Control Limits	Upper Limit	1.12	4.03
	Upper Warning	1.07	3.86
	Lower Warning	0.87	3.16
	Lower Limit	0.82	2.98

Table 7: MLD057 Standards and Controls

Date Range	Standard Cylinder	Control Cylinder
01/01/96 - 09/10/96	NIST15293	C72083
09/12/96 - 11/07/96	NIST9007	C72083
11/18/96 - 03/31/97	NIST15293	C72083
04/01/97 - 09/30/97	NIST15293	AAL3113
10/01/97 - 01/12/98	AAL3113	NIST15293
01/13/98 - 02/09/98	ALM 9015	NIST15293
02/10/98 - 06/30/98	ALM 9015	ALM 9005
07/03/98 - 06/29/99	AAL3113	CC113563
07/07/99 – present	AML29258	CC113563

Figure 1: Pre-Injection Program - Idle State

Time = 0.00 min - 9.10 min

This is the standby/ready position of the GC system.

Note: Valves 2,3, and 4 work in combination.

VALVE STATUS

-1 ---- No sample is spiked
-2 ---- Cryotrap is isolated
-3 ---- Sample flow dead ends and N_2 flows through the MFC
-4 ---- He carrier gas flows through the column

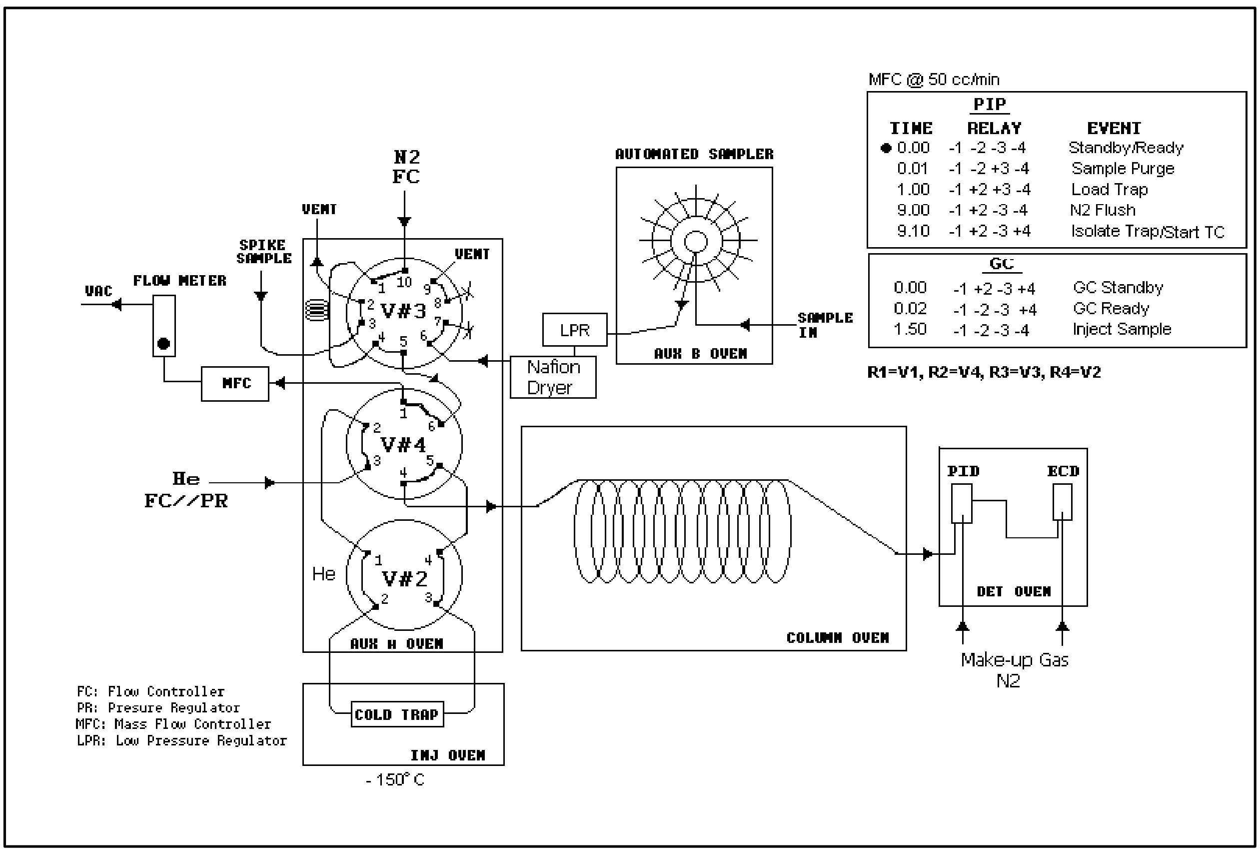


Figure 2: Pre-Injection Program - Purge Sample Line

Time = 0.01 min - 9.09 min

VALVE STATUS

-1 ---- No sample is spiked
-2 ---- Cryotrap is isolated
+3---- Sample flows through to the MFC, purging the sample line
-4 ---- He carrier gas flows through the column

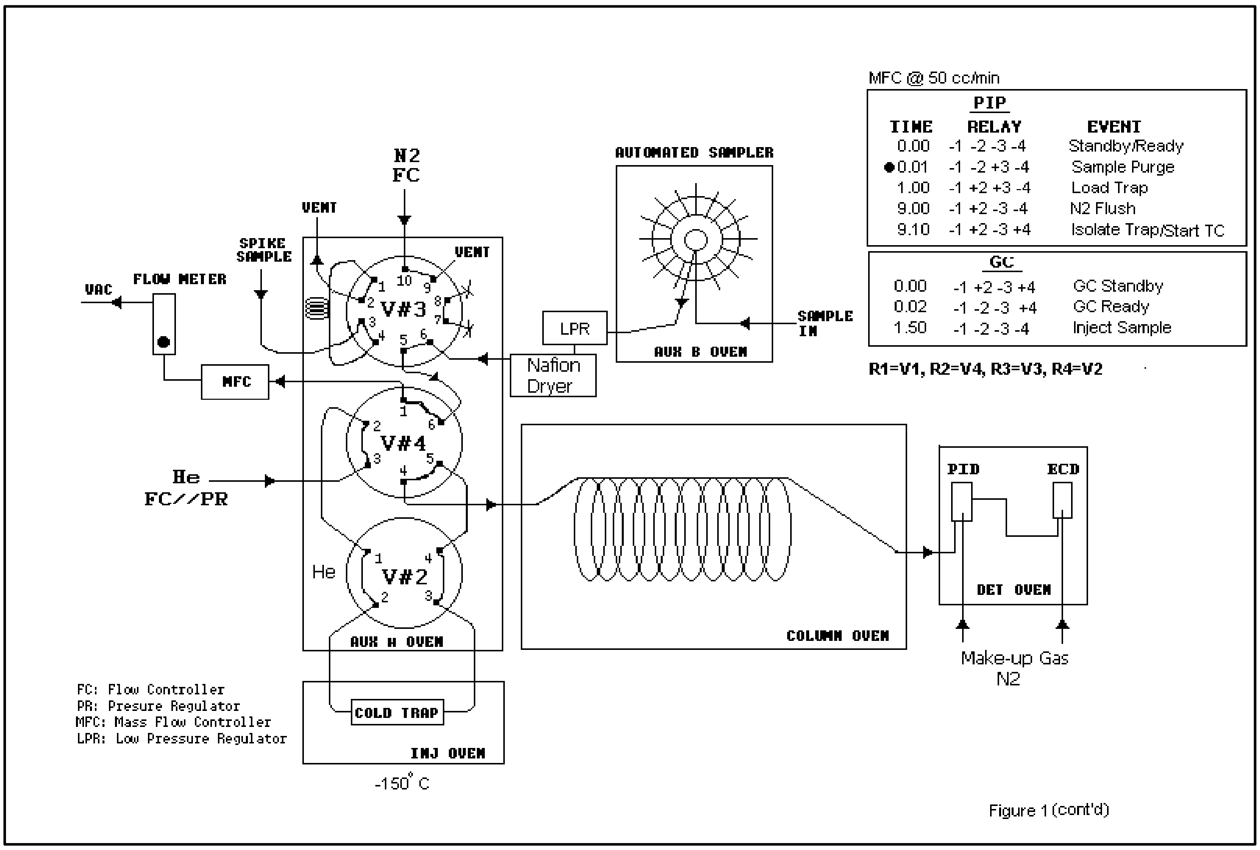


Figure 1 (cont'd)

Figure 3: Pre-Injection Program - Sample Loaded

Time = 1.00 min   -8.10 min

VALVE STATUS

-1 ---- No sample spiked.
+2---- Sample flow is directed through the cryotrap.
+3---- Sample flows through to the MFC and the N_2 flow dead ends.
-4 ---- He carrier gas flows through the column.

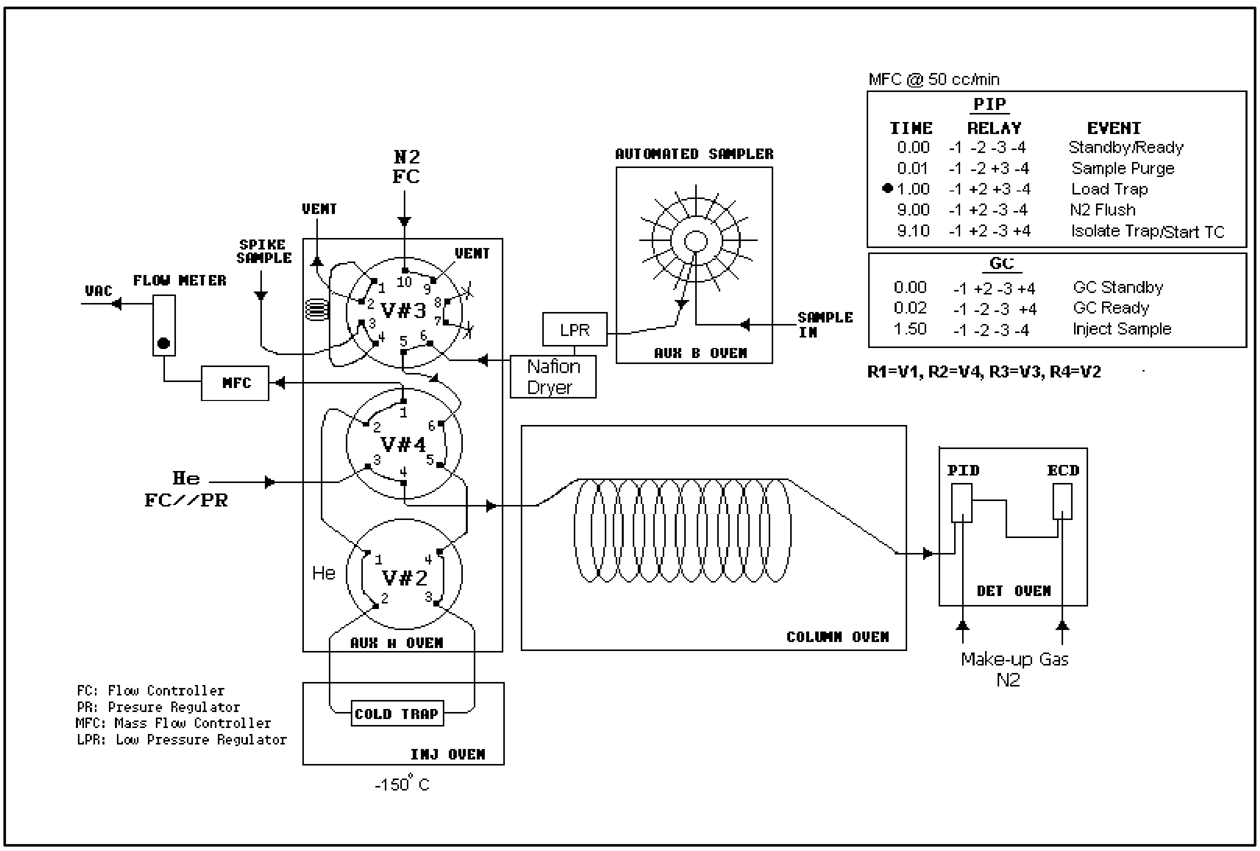


Figure 4: Pre-Injection Program - Sample Loading and Cryotrap Purge

Time = 9.00 min -0.10 min

VALVE STATUS

-1 ---- No sample spiked
+2---- Sample loading is terminated and N_2 flows through cryotrap
-3 ---- Sample flow dead ends and N_2 flows through to the MFC
-4 ---- He carrier gas flows through column

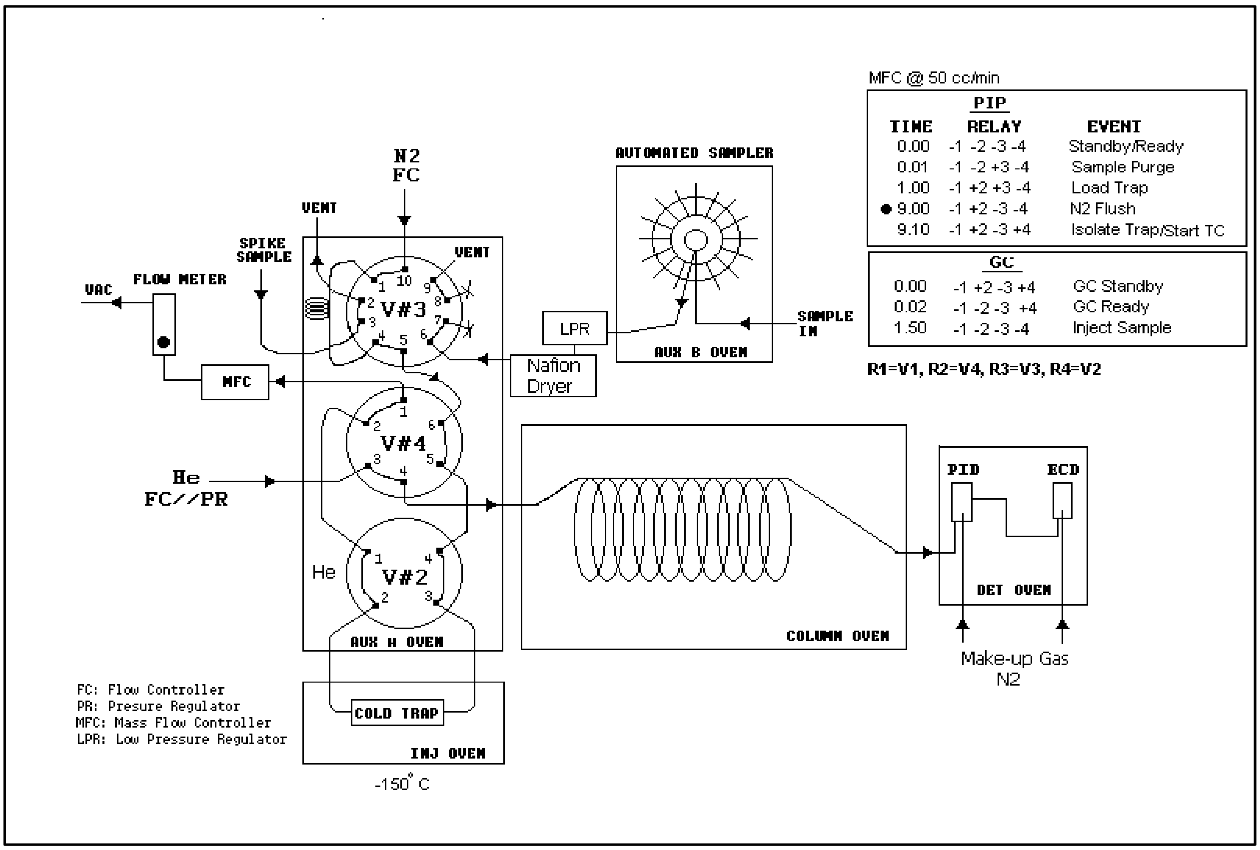


Figure 5: Pre-Injection Program - Injector Isolated for Heating

Time = 9.10 min -0.00 min

VALVE STATUS

-1 ---- No sample spiked
+2---- Sample trap is isolated
-3 ---- Sample flow dead ends and N_2 flows through the MFC
+4---- He carrier gas flows through the column

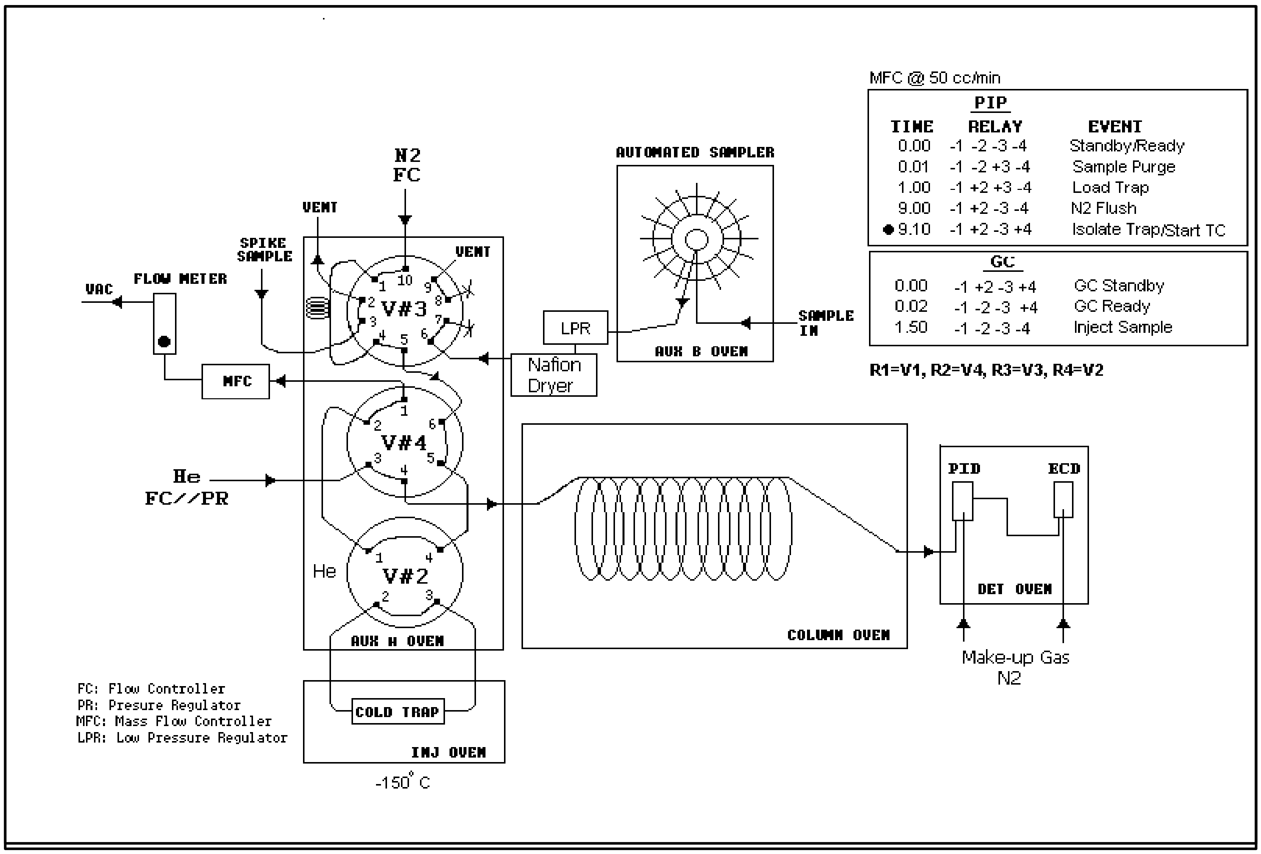


Figure 6: Post-Injection Program - Varian GC Control Started

Time = 0.00 min

Valve Status

-1 ---- No sample spiked
+2---- Sample trap is isolated
-3 ---- Sample flow dead ends and N_2 flows through the MFC
+4---- He carrier gas flows through the column

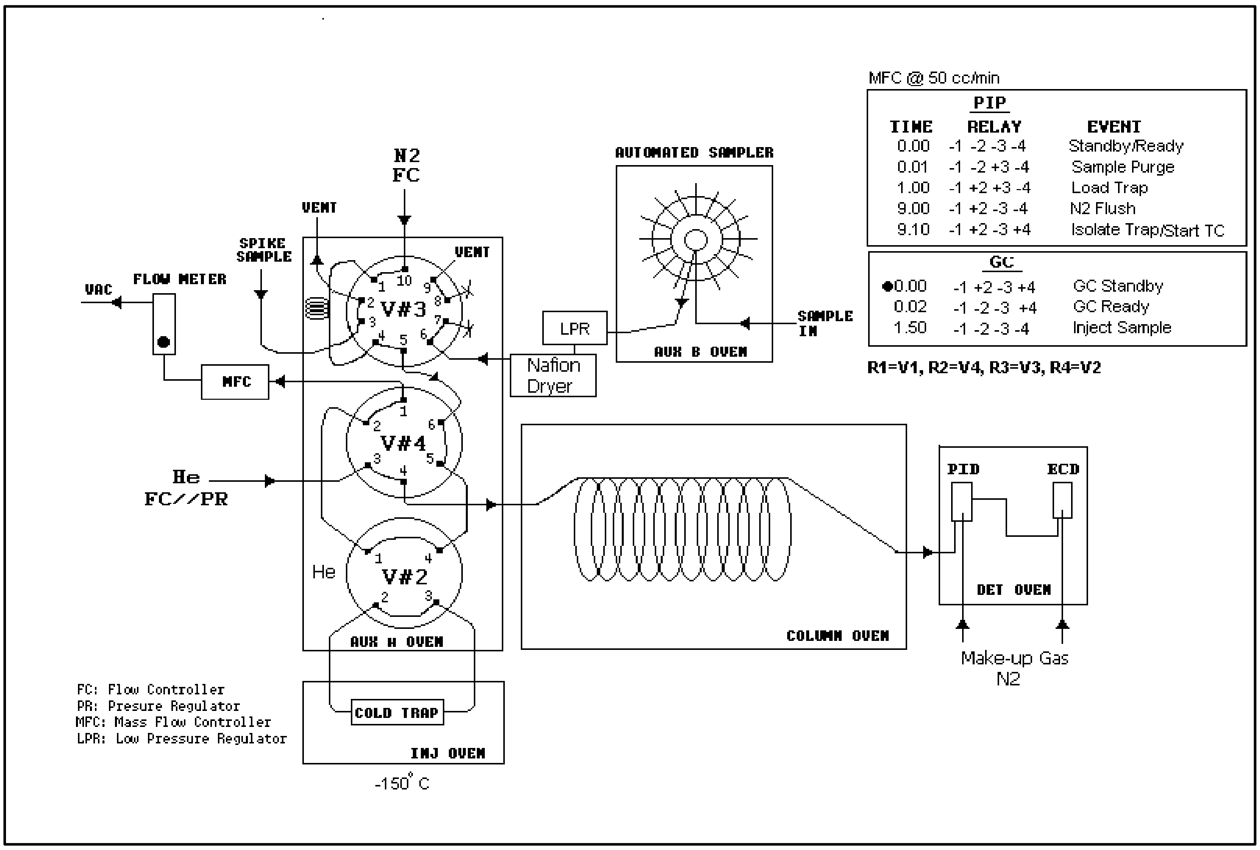


Figure 7: Post-Injection Program - Transition and Cryotrap Pre-Heated

Time = 0.02 min

Valve Status

-1 ---- No sample is spiked
+2---- The cryotrap is isolated
-3 ---- Sample flow dead ends and N_2 flows through the MFC
-4 ---- He carrier gas flows through the column

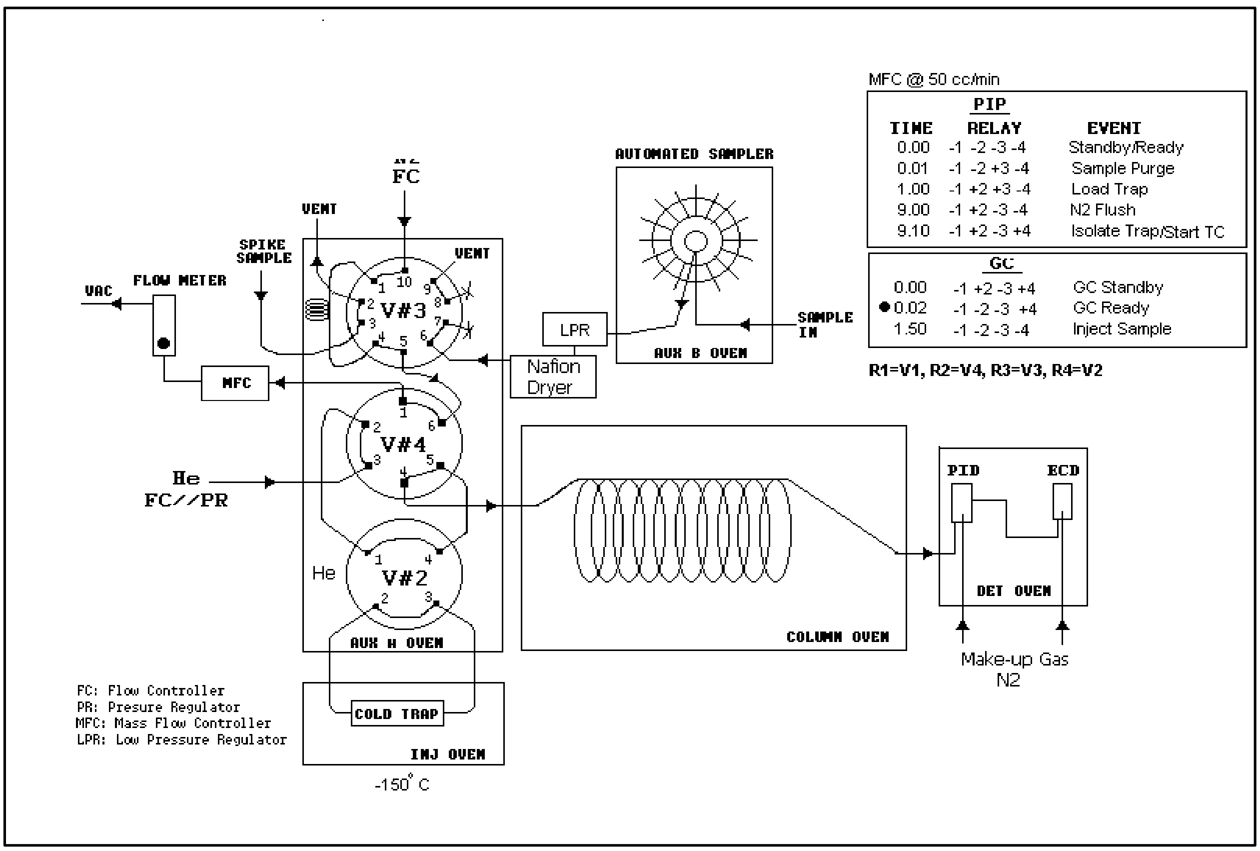


Figure 8: Post-Injection Program - Sample Injected onto the Column

Time = 1.50 min

Valve Status

-1 ---- No sample spiked
-2 ---- He flows through the cryotrap and onto the column
-3 ---- N_2 flows to the MFC
-4 ---- He flows through the cryotrap and onto the column

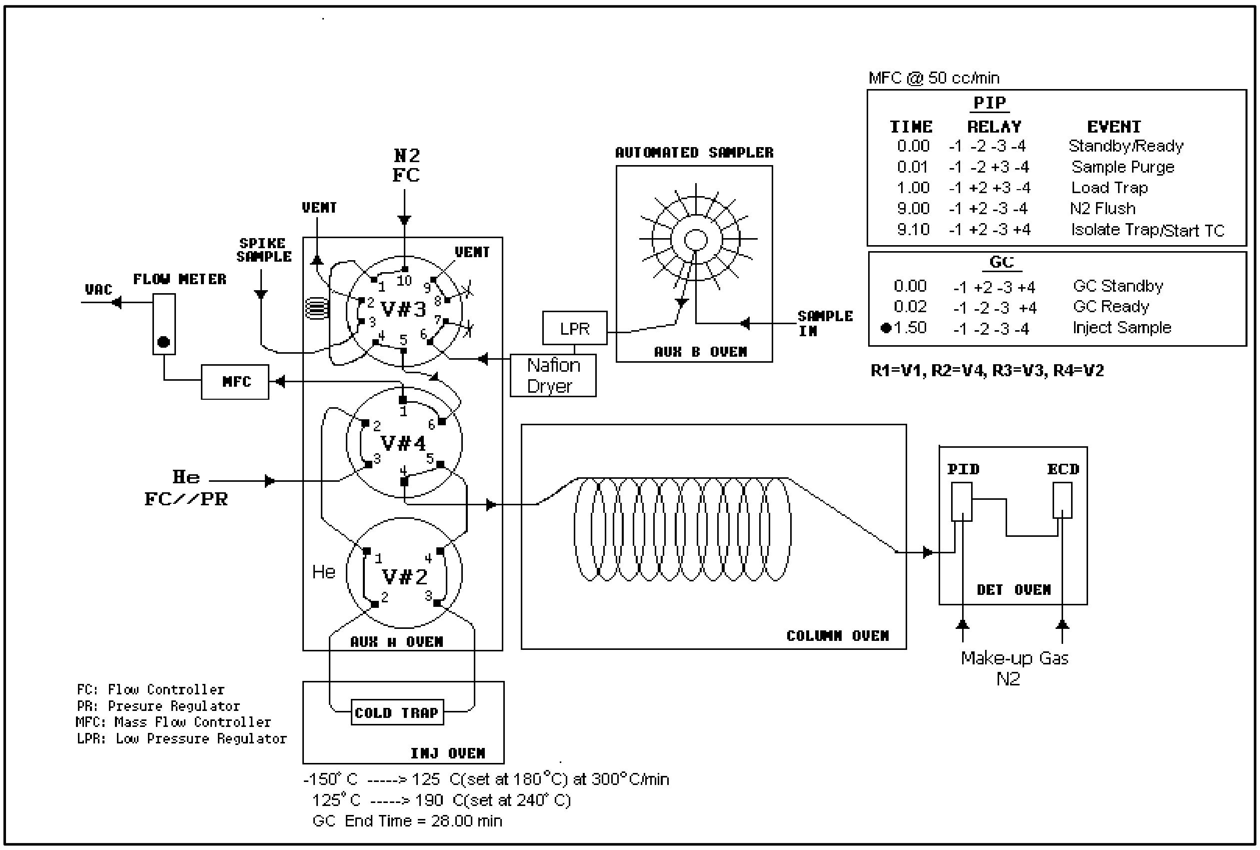


Figure 9: Injector Temperature Conversion

Source: **<u>ULTRA-TRACE HYDROCARBON SYSTEM</u>**
Operator's Manual
Randall Bramston-Cook
Lotus Consulting

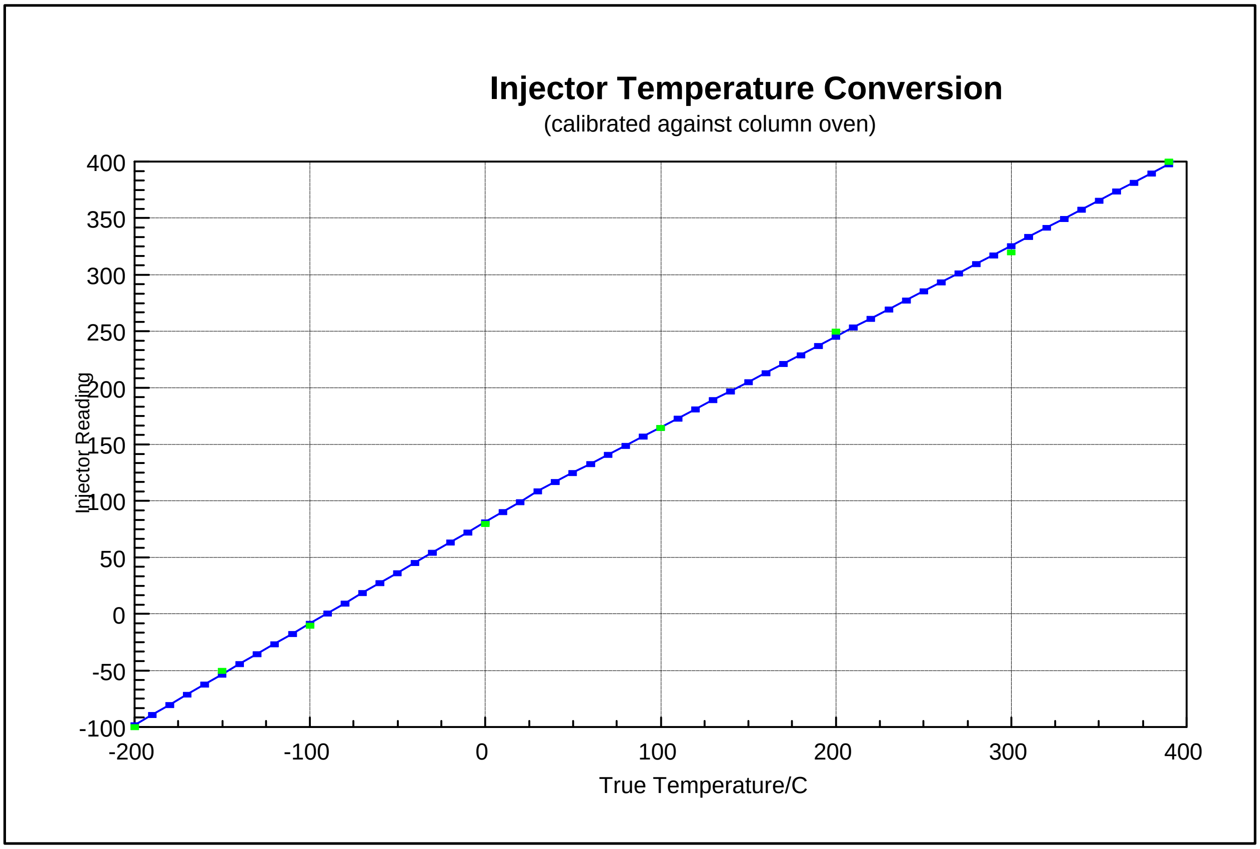
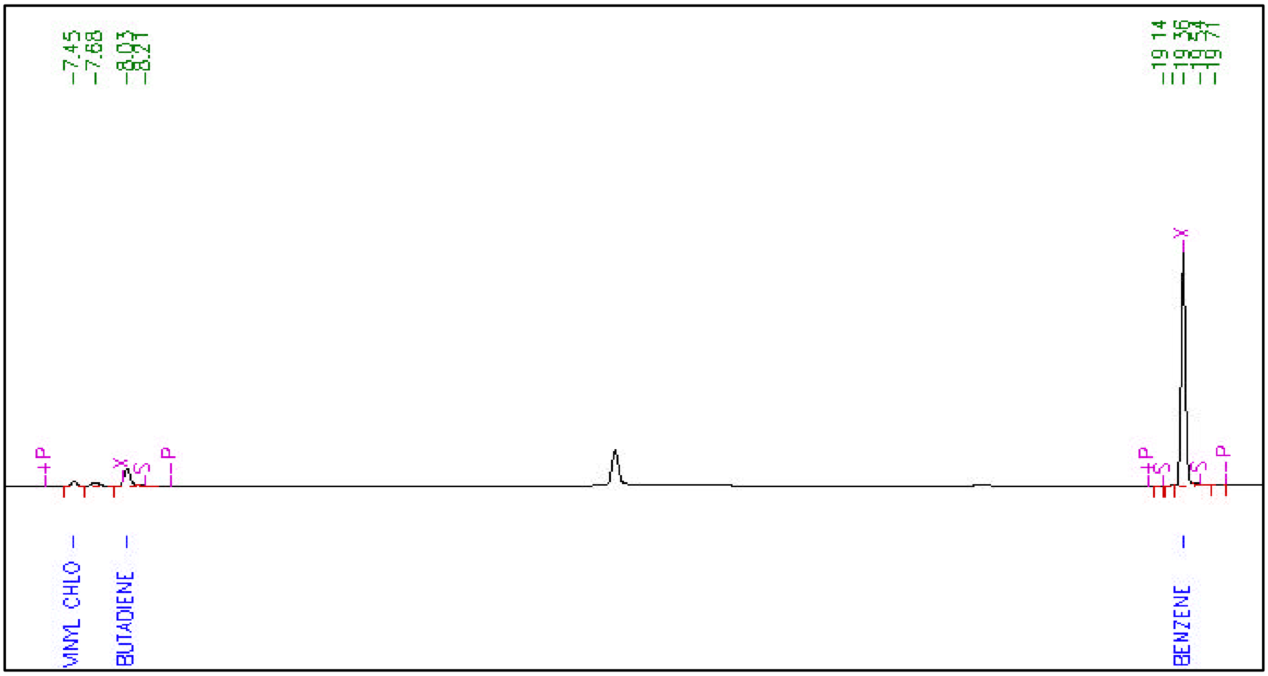


Figure 10: Chromatograms

1. NIST 8399 Traceable Gas Mix Standard



2. Ambient Air Sample Analysis for 1,3 – Butadiene and Benzene

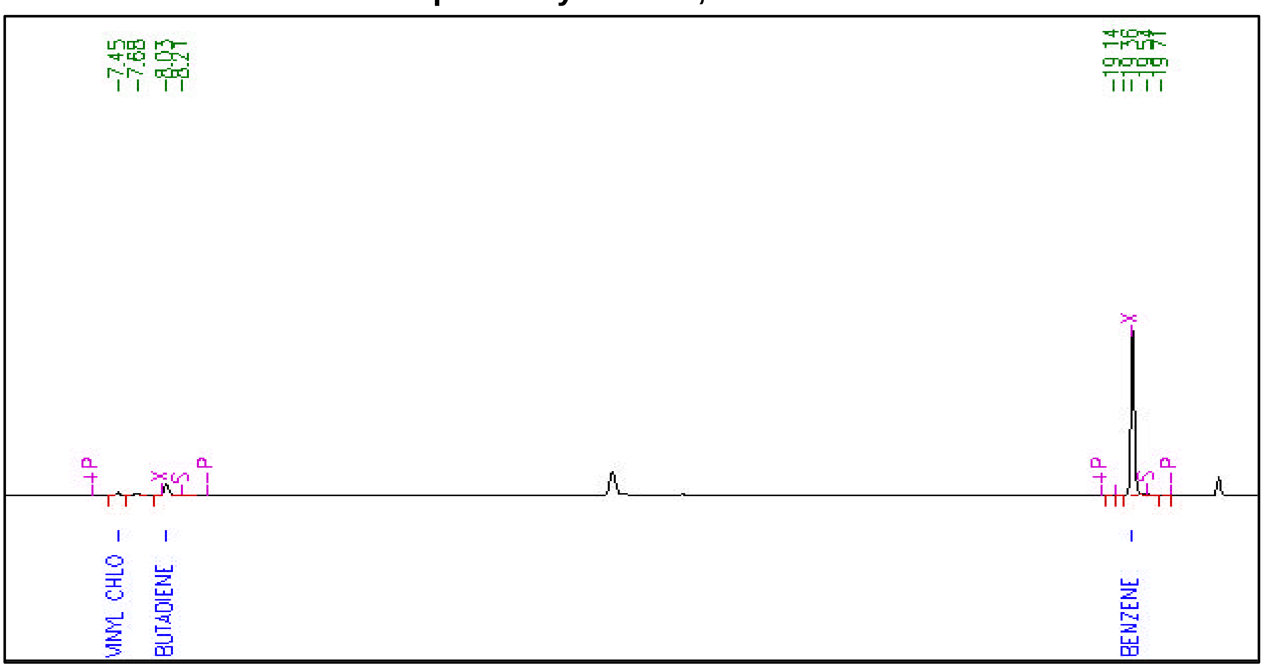


Figure 11: Multipoint Analysis for 1,3-Butadiene

July 8, 1999

1.1 ppbv   Cylinder ALM29258

	Levels of Concentration (ppb)							
Cc	25	50	75	100	200	300	400	500
PPB	0.06880	0.13750	0.20630	0.27500	0.55000	0.83000	1.10000	1.38000
1st	3070	7130	11206	17660	39689	64649	92068	118302
2nd	2928	7097	12243	17397	39510	62670	89940	114839
3rd	2779	7050	11308	16530	37846	60790	88001	105331
4th		7241	11915	16635	37260		85110	101338
Mean	2926	7092	11586	17196	39015	62703	90003	112824
Std Dev	146	40	572	591	1016	1930	2034	6716
% RSD	0.050	0.006	0.049	0.034	0.026	0.031	0.023	0.060
n	3	4	4	4	4	3	4	4

Quadratic Coefficients: $Y=A+BX+CX^2$

Where: A=-3642.5   B=75769.6   C=5431.0

Correlation Coeff. R = 0.9982

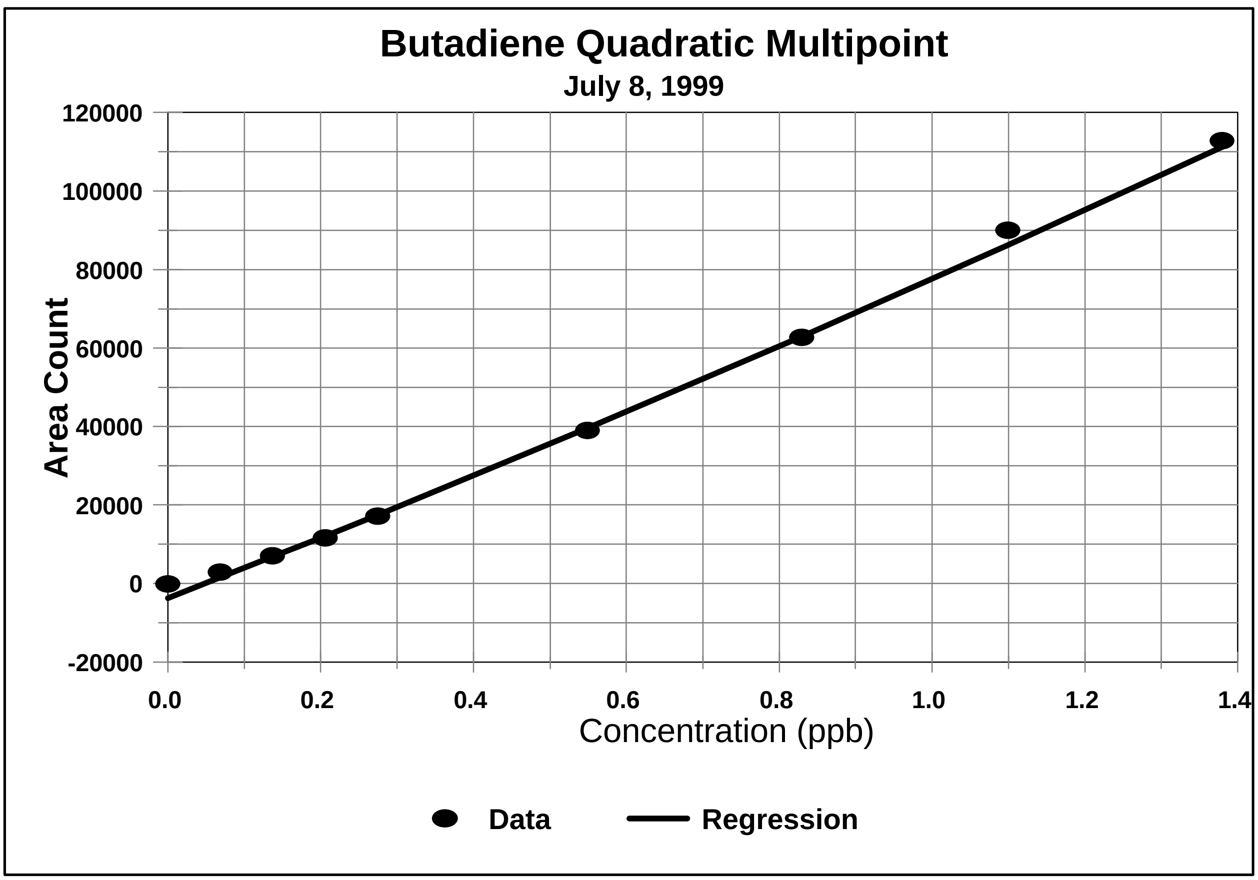


Figure 12: Multipoint Analysis for Benzene

July 8, 1999

5.2 ppbv Cylinder AAL3113

	Levels of Concentration(ppb)								
cc	25	50	75	100	200	300	400	500	600
PPB	0.3250	0.6500	0.9750	1.3000	2.6000	3.9000	5.2000	6.5	7.8
1st	19536	57384	100669	151082	351495	569932	806363	1057409	1309169
2nd	17248	61361	103853	149208	339184	548380	789483	1018191	1262399
3rd	18305	58042	104364	144379	330426	533419	763114	929074	1164641
4th		59107	101298	143934	330366		732787	925484	1149486
Mean	18363	58929	102962	148223	340368	550577	786320	1001558	1245403
Std Dev	1145	2132	2002	3458	10584	18355	21797	65764	73748
% RSD	0.062	0.036	0.019	0.023	0.031	0.033	0.028	0.066	0.059
n	3	3	3	3	3	3	3	3	3

Quadratic Coefficients: $Y= A+BX+CX^2$

Where: A=-32799 B=137341 C=3016

Correlation Coeff. R = 0.9971

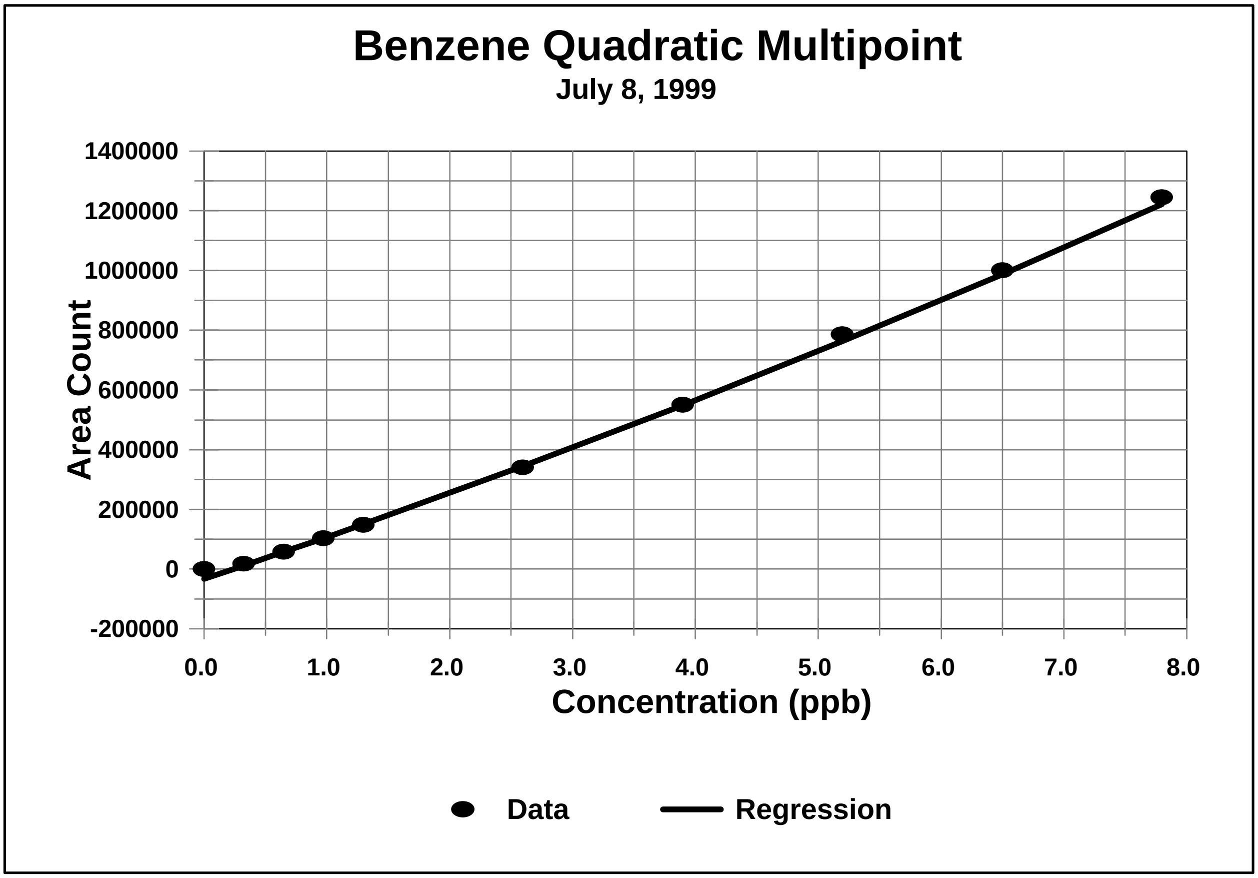
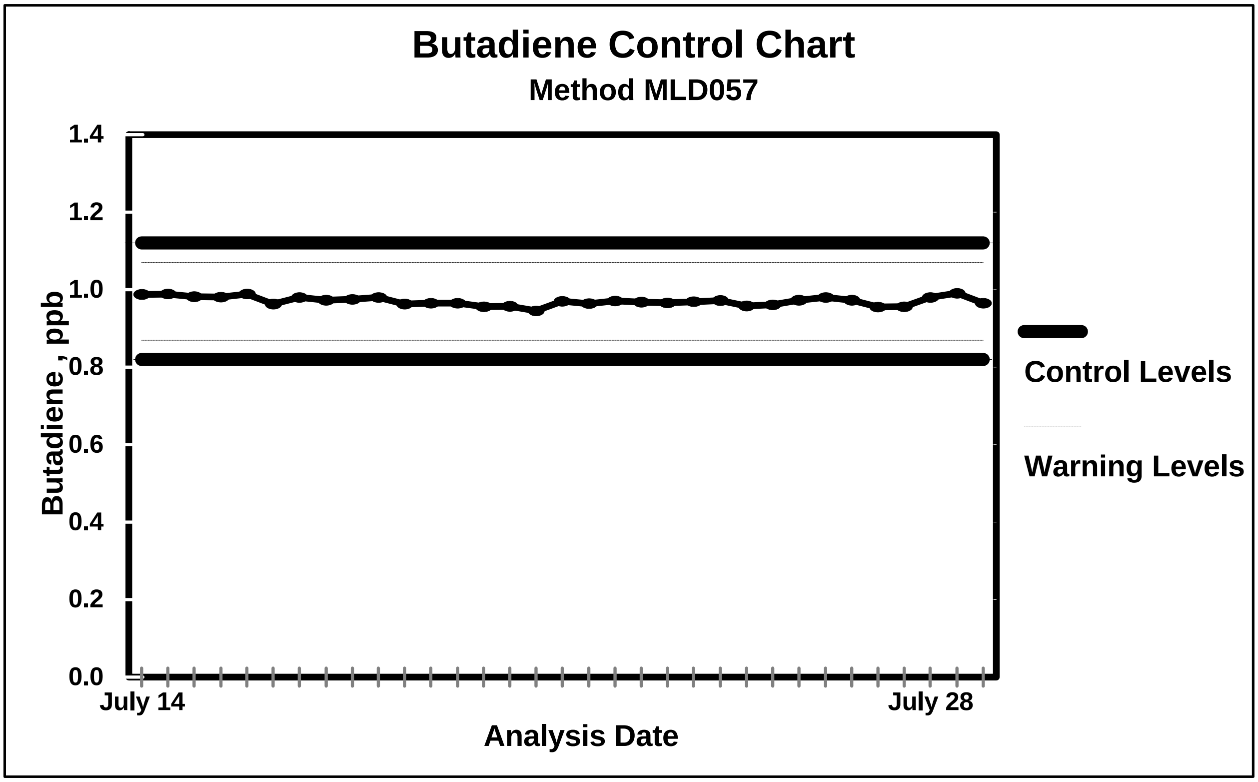
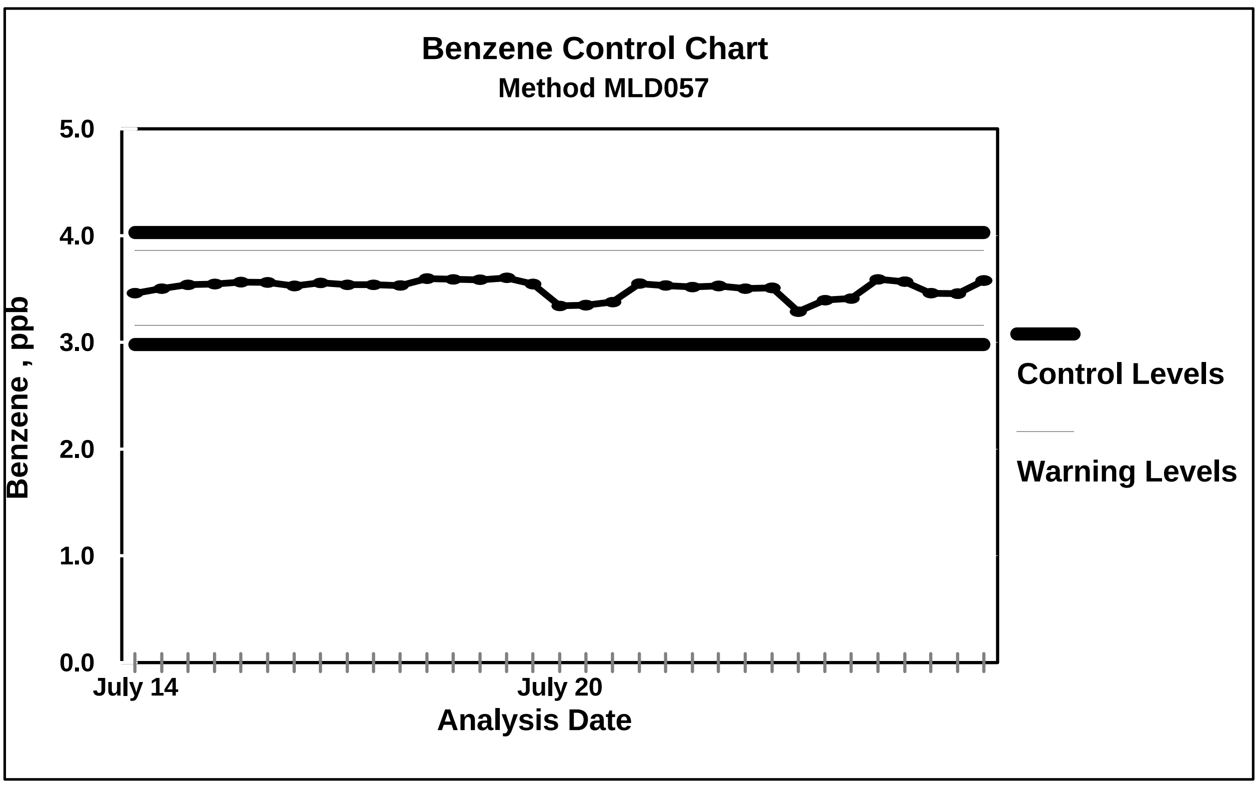


Figure 13: Control Charts





Appendix I

Varian Star Chromatography Workstation

A Varian GC Star Workstation includes an Intel compatible PC, up to four (4) Varian Analog-to-Digital Converter Boards (ADCB), and Varian Star Chromatography software, Version 4.51. The chromatography software operates under Microsoft Windows 9.X or Microsoft Windows NT 4.0. The Star Workstation controls the gas chromatograph, documents the results of chromatographic runs, and is also capable of automating raw data collection and analysis. It is used by the ELB/OLS for automation of the Lotus Consulting/Varian instruments used in the lab. For a more detailed discussion of the Star Workstation software, including setting up methods, sequences, and sample lists, refer to the Star Chromatography Workstation Operational Manual, Varian Chromatography Systems (1993), the Varian GC Star Workstation Manual, and the Ultra-Trace Hydrocarbon System Operator's Manual, by Randall Bramston-Cook.

Although the Star Workstation is capable of data analysis and reporting, Perkin-Elmer (PE) Data Stations running PE's Turbochrom™ software is used for this purpose in the OLS. The reasons include familiarity, smaller data files, and ease in transferring to the Laboratory Information Management System (LIMS). The Star data files are also collected, however, for instrument automation/condition monitoring and as a back up for Turbochrom™ data files.

Each Gas Chromatograph (GC) serviced by the Star Workstation is assigned a separate address, as is each Analog-to-Digital Converter Board (ADCB) installed in the Workstation. Each Workstation can have up to four ADCBs and each ADCB is capable of controlling one instrument and handling two data channels. The address for each ADCB is physically set through DIP switches on the board. Each GC is assigned an address one number greater than it's associated ADCB.

For example, a Varian 3400 GC named BUTADIENE-16/17 is used to analyze butadiene and benzene. The ADCB is configured for address 16 and the attached GC is assigned address 17. It is autocontroled by method MLD57.MTH and is attached to instrument 17. Other methods include IDLE16.MTH for system standby, BAKE16.MTH for conditioning/bakeout of the system, and PURGE16.MTH for autosampler line purging. They are used in automated sequences along with method MLD57.

A copy of the current Star Workstation method, MLD57, is included below. Although there are sections for data handling and reporting, they are not used in this analysis. They are shown in lighter type. Methods IDLE16.MTH, a stand-by method, BAKE16.MTH, a cleaning/conditioning method, are also listed.

Varian Star Workstation Method MLD57.MTH

```
*****************************************************************
Star Chromatography Workstation - Method Listing
Thu Mar 02 17:48:56 2000

Method: C:\STAR\MLD57.MTH
*****************************************************************
**********************
    ADC Board
**********************
Module Address: 16

End Time                      : 24.00 minutes
Autozero at Start             : Yes
Channel A Name                : A
Channel B Name                : B
Channel A Full Scale          : 10
Channel B Full Scale          : 10

Detector Information
--------------------
Detector Bunch Rate           : 16 points (2.5 Hz)
Monitor Length                : 64 bunched points (25.6 seconds)
Data File Name                : mar01
Number Files From             : 1

Integration Parameters        Address 16 Channel A
--------------------------------------------------
Subtract Blank Baseline       : No
Initial S/N Ratio             : 10
Initial Peak Width            : 4 sec
Initial Tangent Height %      : 10%
Monitor Noise                 : Before every run
Measurement Type              : Peak Area
Initial Peak Reject Value     : 500 counts
Report Unidentified Peaks     : No
Report Missing Peaks          : No

Calibration Setup             Address 16 Channel A
--------------------------------------------------
Calculation Type              : % (No Calibration)
Number of Calibration Levels : 3
Curve Origin                  : Include
Curve Fit                     : Linear
Weighted Regression           : None)
Replicate Treatment           : Keep Replicates Separate
Replicate Tolerance           : Always add new replicates
```

```
Out-of-Tolerance Action      : No Action
Calibration Range Tolerance  : 10.0%
Out-of-Tolerance Action      : No Action

Verification Setup           Address 16 Channel A
-------------------------------------------------
Deviation Tolerance          : 100.0%
Out-of-Tolerance Action      : No Action

Peak Table                   Address 16 Channel A
-------------------------------------------------
Reference Peaks Time Windows:Width: 0.10 min. Retention Time 2.0%
Other Peaks Time Windows    :Width: 0.10 min. Retention Time 2.0%

Peak Table Empty

Time Events Table            Address 16 Channel A
-------------------------------------------------
Time Events Table Empty

Report Format: Module ADCB   Address 16 Channel A
-------------------------------------------------
Title                        : MLD51A - Butadiene and Benzene
Print Chromatogram           : No

Print Results                : No
Convert Results to ASCII?    : Off

Calibration Block Reports
Print Report                 : No
Convert Report to ASCII?     : Off

Print Copies                 : 1

**********************
    3400 GC
**********************
Module Address: 17

GC Injector
------------
Injector Type                : Temperature Programmable
GC Injector Oven On?         : Yes
Initial GC Injector Temperature  : -50 degrees C
Initial GC Injector Hold Time    : 0.00 minutes
```

```
Coolant To Injector/Aux. Valve On?:     Yes
Coolant Timeout              : 30.00 minutes

GC Injector Temperature Program 1
-----------------------------------
Final Temperature            : 180 degrees C
Rate                         : 300.0 degrees C / minute
Hold Time                    : 2.00 minutes

GC Injector Temperature Program 2
-----------------------------------
Final Temperature            : 240 degrees C
Rate                         : 300.0 degrees C / minute
Hold Time                    : 25.04 minutes

GC Auxiliary
------------
Injector Type                : Isothermal
GC Auxiliary Oven On?        : Yes
GC Auxiliary Description     : Valves
Initial GC Auxiliary Temperature : 135 degrees C
Initial GC Auxiliary Hold Time   : 0.00 minutes

GC Column
---------
Column Oven On?              : Yes
Initial Column Temperature   : 10 degrees C
Initial Column Hold Time     : 10.00 minutes
Thermal Stabilization Time   : 2.00 minutes

Coolant To Column Valve On?  : Yes
Coolant Timeout              : 30.00 minutes

GC Column Temperature Program 1
--------------------------------
Final Temperature            : 40 degrees C
Rate                         : 50.0 degrees C / minute
Hold Time                    : 1.00 minutes

GC Column Temperature Program 2
--------------------------------
Final Temperature            : 120 degrees C
Rate                         : 8.0 degrees C / minute
Hold Time                    : 1.00 minutes

GC Column Temperature Program 3
```

```
--------------------------------
Final Temperature            : 220 degrees C
Rate                         : 50.0 degrees C / minute
Hold Time                    : 3.40minutes

GC Column A Parameters

Installed?                   : Yes
Length                       : 75.0 meters
Diameter                     : 450 microns
Carrier Gas                  : Helium

GC Column B Parameters

Installed?                   : Yes
Length                       : 75.0 meters
Diameter                     : 450 microns
Carrier Gas                  : Helium

GC Detector Heater
------------------
Detector Heater On?          : Yes
Detector Temperature         : 245 degrees C

GC Detector A
--------------
Detector Type                : PID
Detector On?                 : Yes
Attenuation                  : 8
Detector Range               : 12
Autozero at GC Ready?        : No

GC Detector B
--------------
Detector Type                : ECD
Detector On?                 : No
Attenuation                  : 8
Detector Range               : 10
Autozero at GC Ready?        : Yes

Autosampler
-----------
Autosampler Type             : 8134 SSV

GC Relays
---------
```

Varian Star Workstation Method MLD57.MTH

```
Relay Time Program           : Use
Initial Relay States         : -2-4
Relay Initial Conditions at Run End?: No

Relay Program 1
-----------------
Relay Time:  0.02   State ---4

Relay Program 2
-----------------
Relay Time : 1.50   State ----

GC Stripchart
-------------
Stripchart On?                          : No
```

Varian Star Workstation Method IDLE16.MTH

```
*****************************************************************
Star Chromatography Workstation
Method Listing Fri Mar 03 17:03:53 2000

Method: C:\STAR\IDLE16.MTH
*****************************************************************
**********************
    ADC Board
**********************
Module Address: 16

End Time                     : 30.00 minutes
Autozero at Start            : Yes
Channel A Name               :PID
Channel B Name               : ECD
Channel A Full Scale         : 10
Channel B Full Scale         : 10

Detector Information
--------------------
Detector Bunch Rate          : 2 points (20.0 Hz)
Monitor Length               : 64 bunched points (3.2 seconds)
Data File Name               : idle2
Number Files From            : 1

Integration Parameters Address 16 Channel A
--------------------------------------------
Subtract Blank Baseline      : No
Initial S/N Ratio            : 5
Initial Peak Width           : 4 sec
Initial Tangent Height %     : 10%
Monitor Noise                : Before every run
Measurement Type             : Peak Area
Initial Peak Reject Value    : 1000 counts
Report Unidentified Peaks    : Yes
Report Missing Peaks         : No

Calibration Setup Address 16 Channel A
--------------------------------------
Calculation Type             : % (No Calibration)
Number of Calibration Levels : 10
Curve Origin                 : Force
Curve Fit                    : Linear
Weighted Regression          : (None)
Replicate Treatment          : Keep Replicates Separate
Replicate Tolerance          : Always add new replicates
```

Varian Star Workstation Method IDLE16.MTH

```
Out-of-Tolerance Action      : No Action
Calibration Range Tolerance  : 10.0%
Out-of-Tolerance Action      : No Action

Verification Setup Address 16 Channel A
----------------------------------------
Deviation Tolerance          : 100.0%
Out-of-Tolerance Action      : No Action

Peak Table Address 16 Channel A
--------------------------------
Reference Peaks Time Windows:Width: 0.10 min. Retention Time 2.0%
Other Peaks Time Windows    :Width: 0.10 min. Retention Time 2.0%

Peak Table Empty

Time Events Table Address 16 Channel A
---------------------------------------
Time Events Table Empty

Report Format: Module ADCB Address 16 Channel A
---------------------------------------------------
Title                        :
Print Chromatogram           : Yes
Chromatogram Options         :
Start Retention Time         : 0.00 minutes
End Retention Time:          1440.00 minutes
Length in Pages              : 1
Initial Chart Speed          : 0.0 cm/min
Minutes per Tick             : 1.0
Autoscale                    : On
Time Events                  : On
Chromatogram Events          : On
Retention Times              : On
Peak Names                   : On
Baseline                     : On
Print Results                : Yes
Results Options:
Units                        :
Number of Decimal Digits     : 4
Show Peak Group Totals       : No
Run Log                      : Off
Error Log                    : Off
Calibration Report           : Off
Revision Log                 : On
Notes                        : Off
```

Varian Star Workstation Method IDLE16.MTH

```
Convert Results to ASCII?    : Off

Calibration Block Reports
Print Report                 : No
Convert Report to ASCII?     : Off

Print Copies                 : 1

**********************
    3400 GC
**********************
Module Address: 17
GC Injector
Injector Type                : Temperature Programmable
GC Injector  Oven On?        : Yes
Initial GC Injector Temperature  : 200 degrees C04444
Initial GC Injector Hold Time    : INFINITE

Coolant To Injector/Aux Valve On?: No
Coolant Timeout                  : INFINITE

GC Auxiliary
------------
Injector Type                : Isothermal
GC Auxiliary Oven On?        : Yes
GC Auxiliary Description     : Valving
Initial GC Auxiliary Temperature : 135 degrees C
Initial GC Auxiliary Hold Time   : 0.00 minutes

GC Column
---------
Column Oven On?              : Yes
Initial Column Temperature   : 100 degrees C
Initial Column Hold Time     : INFINITE
Thermal Stabilization Time   : 2.00 minutes

Coolant To Column Valve On?  : No
Coolant Timeout              : INFINITE

GC Column A Parameters
----------------------
Installed?                   : Yes
Length                       : 75.0 meters
Diameter                     : 450 microns
Carrier Gas                  : Helium
```

Varian Star Workstation Method IDLE16.MTH

```
GC Column B Parameters
----------------------
Installed?                    : No
Length                        : 0.0 meters
Diameter                      : 0 microns
Carrier Gas                   : Helium

GC Detector Heater
------------------
Detector Heater On?           : Yes
Detector Temperature          : 245 degrees C

GC Detector A
--------------
Detector Type                 : PID
Detector On?                  : Yes
Attenuation                   : 8
Detector Range                : 10
Autozero at GC Ready?         : Yes

GC Detector B
--------------
Detector Type                 : Not Used
Detector On?                  : No

Autosampler
-----------
Autosampler Type              : 8134 SSV

GC Relays
---------
Relay Time Program            : Use
Initial Relay States          :  -2--
Relay Initial Conditions at Run End?    : Yes

GC Stripchart
-------------
Stripchart On?                : No
```

Varian Star Workstation Method BAKEOU16.MTH

```
*****************************************************************
Star Chromatography Workstation
Method Listing Fri Mar 03 17:04:57 2000

Method: C:\STAR\BAKEOU16.MTH
*****************************************************************
**********************
    ADC Board
**********************
Module Address: 16

End Time                      : 20.20 minutes
Autozero at Start             : Yes
Channel A Name                : A
Channel B Name                : B
Channel A Full Scale          :
Channel B Full Scale          :

Detector Information
--------------------
Detector Bunch Rate           : 16 points (2.5 Hz)
Monitor Length                : 64 bunched points (25.6 seconds)
Data File Name                : star
Number Files From             : 1

Integration Parameters Address 16 Channel A
--------------------------------------------
Subtract Blank Baseline       : No
Initial S/N Ratio             : 5
Initial Peak Width            : 4 sec
Initial Tangent Height %      : 10%
Monitor Noise                 : Before every run
Measurement Type              : Peak Area
Initial Peak Reject Value     : 1000 counts
Report Unidentified Peaks     : Yes
Report Missing Peaks          : No

Calibration Setup Address 16 Channel A
---------------------------------------
Calculation Type              : % (No Calibration)
Number of Calibration Levels : 9
Curve Origin                  : Force
Curve Fit                     : Linear
Weighted Regression           : (None)
Replicate Treatment           : Keep Replicates Separate
Replicate Tolerance           : Always add new replicates
```

Varian Star Workstation Method BAKEOU16.MTH

```
Out-of-Tolerance Action      : No Action
Calibration Range Tolerance  : 10.0%
Out-of-Tolerance Action      : No Action

Verification Setup Address 16 Channel A
----------------------------------------
Deviation Tolerance          : 100.0%
Out-of-Tolerance Action      : No Action

Peak Table  Address 16  Channel A
----------------------------------
Reference Peaks Time Windows:Width: 0.10 min. Retention Time 2.0%
Other Peaks Time Windows    :Width: 0.10 min. Retention Time 2.0%

Peak Table Empty

Time Events Table Address 16 Channel A
-----------------------------------------
Time Events Table Empty

Report Format: Module ADCB Address 16 Channel A
---------------------------------------------------
Title                        : Bakeout Chromatogram – Butadiene
                               Method 57
Print Chromatogram           : Yes
Chromatogram Options:
Start Retention Time         : 0.00 minutes
End Retention Time           : 1440.00 minutes
Length in Pages              : 1
Initial Chart Speed          : 0.0 cm/min
Minutes per Tick             : 1.0
Autoscale                    : On
Time Events                  : On
Chromatogram Events          : On
Retention Times              : On
Peak Names                   : On
Baseline                     : On

Print Results                : No
Convert Results to ASCII?    : Off


Calibration Block Reports
Print Report                 : No
Convert Report to ASCII?     : Off
```

Varian Star Workstation Method BAKEOU16.MTH

```
Print Copies                  : 1

**********************
    3400 GC
**********************
Module Address: 17

GC Injector
------------
Injector Type                 : Temperature Programmable
GC Injector Oven On?          : Yes
Initial GC Injector Temperature  : 200 degrees C
Initial GC Injector Hold Time    : 0.50 minutes

Coolant To Injector/Aux Valve On?  : Yes
Coolant Timeout                  : INFINITE

GC Injector Temperature Program 1
---------------------------------
Final Temperature             : 260 degrees C
Rate                          : 300.0 degrees C / minute
Hold Time                     : 19.50 minutes

GC Auxiliary
------------
Injector Type                 : Isothermal
GC Auxiliary Oven On?         : Yes
GC Auxiliary Description      : Valving
Initial GC Auxiliary Temperature : 135 degrees C
Initial GC Auxiliary Hold Time   : 0.00 minutes

GC Column
---------
Column Oven On?               : Yes
Initial Column Temperature    : 190 degrees C
Initial Column Hold Time      : 0.00 minutes
Thermal Stabilization Time    : 2.00 minutes

Coolant To Column Valve On?   : Yes
Coolant Timeout               : INFINITE
```

Varian Star Workstation Method BAKEOU16.MTH

```
GC Column Temperature Program 1
--------------------------------
Final Temperature             : 200 degrees C
Rate                          : 50.0 degrees C / minute
Hold Time                     : 20.00 minutes

GC Column A Parameters
----------------------
Installed?                    : No
Length                        : 0.0 meters
Diameter                      : 0 microns
Carrier Gas                   : Helium

GC Column B Parameters
----------------------
Installed?                    : No
Length                        : 0.0 meters
Diameter                      : 0 microns
Carrier Gas                   : Helium

GC Detector Heater
------------------
Detector Heater On?           : Yes
Detector Temperature          : 245 degrees C

GC Detector A
--------------
Detector Type                 : PID
Detector On?                  : Yes
Attenuation                   : 8
Detector Range                : 10
Autozero at GC Ready?         : No

GC Detector B
--------------
Detector Type                 : ECD
Detector On?                  : No
Attenuation                   : 8
Detector Range                : 1
Autozero at GC Ready?         : No

Autosampler
-----------
Autosampler Type              : 8134 SSV
```

Varian Star Workstation Method BAKEOU16.MTH

```
GC Relays
---------
Relay Time Program           : Use
Initial Relay States         :  ----
Relay Initial Conditions at Run End?    : No

GC Stripchart
-------------
Stripchart On?               : No
```

APPENDIX II

Additional Setpoints

GC Column Stand by Temperature-------150 ºC

He Carrier Gas:

Set to 5.00 cm^3/minute
Flow Controller----------------------------Set digital gauge at 2.00 (~ cm^3/minute)
Pressure Regulator ----------------------Set analog gauge to 49.8 psi

N_2 Make-up Gas:

PID ---------------------------------- Set N_2 flow to 13.00 cm^3/minute
ECD -------------------------------------Set N_2 flow to 17.00 cm^3/minute
The ECD is in series with the PID. It is not used in this method.

Total He and N_2 Gas Flow ----------------35.00 cc/minutes

N_2 Purge Gas:

Flow Controller----------------------------Set digital gauge at 35.0 (~ cm^3/minute)
N_2 purge Pressure Gauge -------------Reads > 60 psi

Mass Flow Controller (MFC):

Set sampling flow rate to 50 cm^3/minute
Set --------------------------------------49.9% of full scale
Read --------------------------------------50.0% of full scale
--------------------------------------100 cm^3/minute equals 100% full scale

Required Regulator Pressures:

He - Carrier Gas-------------------------------80 psi

N_2 - Valve Actuator Gas --------------------80 psi

N_2 - Make-up Gas-----------------------------80 psi

N_2 – Dryer Purge Gas -----------------------80 psi

APPENDIX III

Perkin-Elmer Nelson Turbochrom Data System

Data Station

The Perkin-Elmer (PE) Data Station includes an Intel based PC and PE-Nelson 2700/Turbochrom™ Chromatography software, and one or more PE-Nelson Model 970 Analog/Digital Converters. Up to 15 A/D converters can be attached to a single Data Station. In practice, only two (2) to four (4) A/Ds are used per Data Station. Each A/D can support two synchronous analog data channels.

The PE-Nelson 2700/Turbochrom™ Chromatography software, Version 4.1.2 <2F12>, operates under Microsoft Windows 9.x, but will not function under the Windows NT. For a more detailed discussion of the Turbochrom™ software, please refer to the Turbochrom User's Guide, Volumes 1 and 2.

File Naming Conventions

Turbochrom™ uses the first four (4) characters to form a data files base name. A three-digit cycle number is then appended to the selected base name and the data files are stored in a specified directory. The same base name is used for storing raw, result, baseline, and modified raw files, but the three-character cycle number differentiates one file from another. If a duplicate file name exists, the system will rename the current sample by appending letters. This will cause problems with the eventual transfer of data to LIMS. To prevent this and to allow easy identification of data, the following naming convention is used:

1. Use only a 4 character base name for data runs.
2. The first two characters are the month code.
3. The third and fourth characters are the date code
4. The fifth through seventh characters are automatically assigned by the data system.

The applicable month codes are:

January	=	JA	May	=	MY	September	=	SE
February	=	FB	June	=	JN	October	=	OC
March	=	MR	July	=	JL	November	=	NV
April	=	AP	August	=	AG	December	=	DC1

For example:

FB 01 020 = FEBRUARY 1st , RUN #20

Month Code	Day Code	Cycle No.
FB	01	020

Sample Naming Conventions

Within a sequence or during a manual download, a sample name this must be entered. The sample name must be uniquely formatted for LIMS to recognize.

- Enter a system blank as: **Blank**
- Enter a Calibration standard as: **ALM29258 or XLM20258**
- Enter a control sample as: **C113563 or XC113563**

Ambient air samples are assigned an 8-character bar code number. When logged into the LIMS, it receives a 9-digit number that starts with a 2. For Toxics, the bar code number begins with TX, followed by 6 digits. The sample name, for Turbochrom™, includes the bar code number, plus a site code. A space is used to separate the bar code section used for LIMS and the site information. A typical sample name would be entered as:

TX001259 MX

A duplicate, or replicate analyses, receives an additional alpha character, A through J, at the end of the bar code number. A through J represents the 2^{nd} through 10^{th} replicates. The duplicate for the above sample would be entered as:

TX001259A MX

Turbochrom Set-Up

The method file, MLD57A.MET follows.

```
Turbochrom Method File: C:\TC4-2F12\MLD57.MTH
Created by  : HML          on : 11/6/98   10:11 AM
Edited by   : Ferry/ FNN   on :  3/2/00   10:20 AM
Description :

Number of Times Edited     : 82
Number of Times Calibrated : 2407

Instrument Conditions :
     7/3 Switched relay 2 & 4. (EMcC/MRP)
     MLD51A.MTH runtime 30 min, multiple level cals,
     new cal std, new baseline events

Instrument Control Method:
     Instrument name : 970_BUTADIENE

Interface Parameters  :
     Delay Time           : 0.00 min.
     Run Time             : 30.00 min.
     Sampling Rate        : 2.0000 pts/s
     Interface Type       : 900
     Analog Voltage Input : 1000 mV
     Data will be collected from channel A

Timed Events:
     There are no timed events in the method

Real Time Plot Parameters :
     Channel A -- Pages: 1   Offset: 0.000 mV  Scale: 10.000 mV
     Channel B -- Pages: 1   Offset: 0.000 mV  Scale: 1000.000 mV

Processing Parameters :
      Bunch Factor    : 1 points
      Noise Threshold : 1 uV
      Area Threshold  : 25.00 uV
      Peak Separation Criteria
      Width Ratio             : 0.200
      Valley-to-Peak Ratio  : 0.010
      Exponential Skim Criteria
      Peak Height Ratio     : 5.000
      Adjusted Height Ratio : 4.000
      Valley Height Ratio   : 3.000

Baseline Timed Events :
      Event #1 - -P  at  0.100
      Event #2 - +P  at  7.150
      Event #3 -  S  at  8.047
      Event #4 - +X  at  8.204
```

```
      Event #5 -  S  at  8.447
      Event #6 - -P  at  8.500
      Event #7 - +P  at 19.000
      Event #8 -  S  at 19.285
      Event #9 - +X  at 19.553
      Event #10 - S  at 19.885
      Event #11 --P  at 19.945

Annotated Replot Parameters :
      Offset will be autozeroed
      Plot Scale       : 35.000 mV
      Number of Pages  : 1
      Plot Title       : Chromatogram
      X-Axis Label     : Time [min]
      Y-Axis Label     : Response [mV]
      Orientation      : Landscape
      Retention Labels : Top of Plot
      Component Labels : Actual Time
      Start Time       : 0.00
      End Time         : 30.00

Report Format files :
      No report format files given

User Programs :
      No user programs will be executed

Global Information :
      Default Sample Volume : 1.000 ml
      Quantitation Units    : ppb
      Void Time             : 0.000 min
      Correct amounts during calibration : YES
      Reject outliers during calibration : NO
      An External Standard calibration will be used
      Unknown peaks will use the response factor of the nearest
        component

  Component Information :
      Vinyl Chloride
         Component Type     : Single Peak Component
         Retention Time     : 7.571 min
         Search Window: 0.00 s, 1.30 %
         Reference Component:
         Find peak closest to expected RT in window
         Calibrating Area versus Amount using a 2nd Order Fit
         Curve will be forced through the origin
         Amounts will not be scaled prior to the regression
         Weighting factor for the regression: None
```

User Values:
Label :
Value 1: 0.000000
Value 2: 0.000000
Value 3: 0.000000
Value 4: 0.000000
Value 5: 0.000000
Calibration Levels:

Level Name	Amount	Area	Height	ISTD Re
50	0.2050	739.50	175.04	----------
100	0.4100	1437.00	356.00	----------
400	1.6400	6750.41	1713.01	----------

Calibration Curve:$y= (0.000000) + (3360.531646)x + (460.471100)x^2$
R-squared : 0.999939

Butadiene
Component Type : Single Peak Component
Retention Time : 8.177 min
Search Window: 0.00 s, 2.00 %
Reference Component:
Find peak closest to expected RT in window
Calibrating Area versus Amount using a 2nd Order Fit
Curve will be forced through the origin
Amounts will not be scaled prior to the regression
Weighting factor for the regression: None
User Values:
Label :
Value 1: 0.000000
Value 2: 0.000000
Value 3: 0.000000
Value 4: 0.000000
Value 5: 0.000000
Calibration Levels:

Level Name	Amount	Area	Height	ISTD Re
50	0.1380	2182.00	473.60	----------
100	0.2750	5062.50	1096.04	----------
400	1.1000	26932.00	5785.37	----------
500	1.3800	34776.00	7492.71	----------

Calibration Curve:$y=(0.000000) + (18167.096115)x + (5275.56425)x^2$
R-squared: 0.999064

Benzene
Component Type : Single Peak Component
Retention Time : 19.390 min
Search Window: 0.00 s, 1.50 %

```
        Reference Component:
        Find largest peak in window
        Calibrating Area versus Amount using a 2nd Order Fit
        Curve will be forced through the origin
        Amounts will not be scaled prior to the regression
        Weighting factor for the regression: None
        User Values:
               Label  :
               Value 1: 0.000000
               Value 2: 0.000000
               Value 3: 0.000000
               Value 4: 0.000000
               Value 5: 0.000000
        Calibration Levels:
  Level Name    Amount       Area         Height          ISTD Re
-----------------------------------------------------------------
     50         0.6500       18766.50       5379.35     ----------
    100         1.3000       41897.75      13079.19     ----------
    400         5.2000       222028.88     70972.46     ----------
    500         6.5000       283312.50     91407.00     ----------
```

Calibration Curve:y=(0.000000) + (32437.864321)x + (1787.39247)x^2

```
R-squared : 0.998938

  Calibration Replicate Lists:
  Component: Vinyl Chloride
     Level : 50
  Area     Height  Vol Adj Amt ISTD Response  ISTD Amount
  Date/Time
-----------------------------------------------------------------
  739.50   175.04   0.2050   ----------       ----------   3/2/00
     Level : 100
  Area     Height  Vol Adj Amt ISTD Response  ISTD Amount
  Date/Time
-----------------------------------------------------------------
 1437.00   356.00   0.4100   ----------       ----------   3/2/00
     Level : 400
  Area     Height  Vol Adj Amt ISTD Response  ISTD Amount
  Date/Time
-----------------------------------------------------------------
 6750.41  1713.01   1.6400   ----------       ----------   3/2/00


  Component: Butadiene
     Level : 50
  Area     Height  Vol Adj Amt ISTD Response  ISTD Amount
  Date/Time
-----------------------------------------------------------------
```

```
 2182.00   473.60    0.1380   ----------       ----------  3/2/00
     Level : 100
  Area     Height  Vol Adj Amt ISTD Response  ISTD Amount
  Date/Time
------------------------------------------------------------------
 5062.50  1096.04    0.2750   ----------       ----------  3/2/00
     Level : 400
  Area     Height  Vol Adj Amt ISTD Response  ISTD Amount
  Date/Time
------------------------------------------------------------------
26932.00  5785.37    1.1000   ----------       ----------  3/2/00
     Level : 500
  Area     Height  Vol Adj Amt ISTD Response  ISTD Amount
  Date/Time
------------------------------------------------------------------
34776.00  7492.71    1.3800   ----------       ----------  3/2/00

  Component: Benzene
     Level : 50
  Area     Height  Vol Adj Amt ISTD Response  ISTD Amount
  Date/Time
------------------------------------------------------------------
18766.50  5379.35    0.6500   ----------       ----------  3/2/00
     Level : 100
  Area     Height  Vol Adj Amt ISTD Response  ISTD Amount
  Date/Time
------------------------------------------------------------------
41897.75 13079.19    1.3000   ----------       ----------  3/2/00
     Level : 400
  Area     Height  Vol Adj Amt ISTD Response  ISTD Amount
  Date/Time
------------------------------------------------------------------
222028.88 70972.46   5.2000   ----------       ----------  3/2/00
     Level : 500
  Area     Height  Vol Adj Amt ISTD Response  ISTD Amount
  Date/Time
------------------------------------------------------------------
283312.50    91407.00 6.5000    ----------    ----------    3/2/00
```